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ABSTRACTS OF CURRENT PUBLISHED INFORMATION ON NICKEL AND ITS ALLOYS

GENERAL

Precipitation from Solid Solution: Educational Lectures

AMER. SOC. METALS: 'Precipitation from Solid Solution.'

Published by the Society, 1959; 517 pp. Price $10.00.

The volume contains the series of nine educational lectures on precipitation from solid solution which were presented to members of the American Society for Metals during the National Metal Congress and Exposition, Chicago, November 1957.

The introductory lecture, which discusses the theory, mechanism and kinetics of precipitation, is followed by eight papers concerned with precipitation reactions in various classes of commercially available age-hardening alloys and steels. In format the papers are basically identical: the scope of the information is outlined, phasial equilibria of pertinent alloy systems are discussed, and finally the heat-treatment, working, and properties of the respective classes of materials are reviewed. Discussion in each of the monographs is supported by numerous graphical and tabular data and, wherever relevant, by photomicrographs.

The papers contained in the volume are listed below:

R. F. MEHL: 'Introduction and Summary', pp. 1-5.

J. B. NEWKIRK: 'General Theory, Mechanism and Kinetics', pp. 6-149.
Bibliography: 379 items.

W. A. ANDERSON: 'Precipitation - Hardening Aluminium-base Alloys', pp. 150-207.
Bibliography: 49 items.

H. W. PAXTON: 'Precipitation Reactions in Irons and Low-Alloy Steels', pp. 208-43.
Bibliography: 71 items.

A. J. LENA: 'Precipitation Reactions in Iron-base Alloys', pp. 244-327.
Bibliography: 94 items.

W. D. ROBERTSON and R. S. BRAY: 'Precipitation Hardening of Copper Alloys', pp. 328-90.
Bibliography: 138 items.

R. S. BUSK: 'Magnesium Alloys', pp. 391-416.
Bibliography: 28 items.

C. G. BIEBER and R. J. RAUDEBAUGH: 'Some Age-Hardening Characteristics of Nickel-Chromium Alloys (Nickel-Rich) containing Aluminium and Titanium', pp. 417-48.
Bibliography: 21 items.

G. A. GRITZLEN, W. H. FAULKNER, B. R. BARRETT and R. W. FOUNTAIN: 'Precipitation in Cobalt-base Alloys', pp. 449-94.
Bibliography: 52 items.

NICKEL

Extraction of Nickel and Cobalt: Bibliography

C. A. JONES: 'Bibliography on Extractive Metallurgy of Nickel and Cobalt, 1900-1928.'

U.S. Bur. Mines, Information Circular 7883, 1959; 33 pp.

This *bibliography*, prepared as part of the U.S. Bureau of Mines research programme on Cuban lateritic and serpentine ores, supplements that covering relevant literature published in the period 1929-55 (see abstract in *Nickel Bulletin*, 1958, vol. 31, No. 3, p. 68).

The present volume extends the coverage to the earliest years of nickel and cobalt metallurgy. The 344 annotated abstracts are grouped, according to their subject matter, in five sections concerned with general metallurgy, pyrometallurgical, hydrometallurgical, and electrometallurgical processes, and miscellaneous information. Each section is suitably sub-divided.

Refining of Nickel/Copper/Cobalt Mattes

R. F. PEARCE, J. P. WARNER and V. N. MACKIW: 'Refining of Nickel, Copper, Cobalt Mattes by Pressure Leaching and Hydrogen Reduction.'

Amer. Inst. Mining, Metallurgical and Petroleum Engineers, Annual Meeting, 1959, *Preprint* 59B41; 24 pp.

Pressure leaching is employed in the refining of various metals, but, until relatively recently, only for treatment of flotation concentrates or the original ores. Development work by Sherritt Gordon Mines, Ltd. has extended the use of the technique to processing of enriched products, in particular, to treatment of mattes. Investigations have been in progress since, in 1949, a nickel/copper/cobalt matte was successfully leached. This paper, which is based on the results of laboratory and pilot-plant investigations, reviews the processing conditions which have been found optimum for production of high-purity

metals from various grades of nickel/copper/cobalt mattes.

The hydrometallurgical processes developed by the Company involve three main stages. In the first stage the un-refined material is leached so that the valuable metals go into solution, while, as far as possible, the impurities in the concentrate are left in the insoluble residue. The next stage comprises purification of the solution derived from the liquid/solid separation which follows the leaching step, and finally this solution is treated for recovery of the metals. The modifications involved in the application of these processes to refining of mixed mattes are outlined in three sections. In the first, factors influencing choice of ammonia or acid leaching are discussed, and, with the aid of flow sheets, a description is given of the procedures developed for the following grades of matte: nickel, nickel/iron, nickel/copper, nickel/cobalt, and nickel/cobalt/iron. The second section contains a discussion of the factors associated with leaching, and a review of the methods used to purify the leaching solution. In the final section consideration is given to recovery of the metal by hydrogen reduction.

See also:

Separation of Nickel and Cobalt in the Refining of Lateritic Ores.

J. F. SHEA and O. F. TANGEL: 'Large-Scale Laboratory Investigation of the Ammonium Sulphate Leaching-Hydrogen Reduction Process as Applied to Nicaro Bulk Precipitate.'

Amer. Inst. Mining, Metallurgical and Petroleum Engineers, Annual Meeting, 1959, *Preprint* 59*B*113; 24 pp.

The investigation described was carried out, under the aegis of the U.S. General Services Administration, at Battelle Memorial Institute, with the aim of developing a nickel/cobalt separation process capable of being integrated into the refining procedure used at the Nicaro (Cuba) nickel plant.

When the investigation was started, the procedure used at the plant involved reducing and leaching the ore and boiling the pregnant solution to produce a so-called 'bulk precipitate' which contained virtually all of the nickel and cobalt dissolved in the leaching stage. To meet specifications, the weight ratio of nickel to cobalt in the finished product had to be at least 100 to 1. The ratio of the two metals in the Nicaro ore was approximately 15 to 1 and, since the refining process included no nickel/cobalt separation step, the specified ratio could be achieved only by adjusting the roasting and leaching conditions so as to permit selective leaching of the nickel and rejection of most of the cobalt with the tailings, a procedure which resulted in reduced nickel recovery.

Following research at Battelle Memorial Institute, it was suggested that an appropriate solution to the problem would be to re-process the bulk precipitate, using ammonium-sulphate-leaching and hydrogen-reduction techniques based on those developed by Sherritt Gordon Mines, Ltd. Details of the recommended processes are given by the authors.

(An investigation germane to that described is referred to in *Nickel Bulletin*, 1958, vol. 31, No. 12, p. 314.)

Influence of Cold-Drawing and Annealing on the Modulus of Rigidity of Nickel, 'Monel' and 'CA Alloy'

H. TAKEI: 'The Effects of Cold-Drawing and Annealing on the Rigidity Modulus in Nickel, 'Monel' and 'CA Alloy.'

Jnl. Japan Inst. Metals, 1958, vol. 22, Aug., pp. 428–32.

Changes in the modulus of rigidity, electrical resistivity and hardness of nickel, 'Monel' and the 'CA Alloy' (copper 91·34, aluminium 3·96, nickel 3·68, silicon 0·7, zinc 0·25, titanium+iron 0·03, per cent.), were determined as a function of cold-drawing and annealing. The measurements were carried out on wire specimens 0·6 mm. in diameter, using a torsion pendulum, a potentiometer and a microhardness tester. The moduli of rigidity of nickel and 'Monel' were found to decrease considerably with cold-drawing up to a reduction-in-area of 80 per cent.; at higher reductions the values obtained gradually increased. A slight increase in the moduli of the two materials was observed after annealing in the range 200°–300°C., but the values after treatment at 500°–650°C. were remarkably high. Cold-working had relatively little effect on the modulus of rigidity of 'CA Alloy'. Annealing at temperatures in the range of 100°–250°C. proved only slightly beneficial. The values obtained at higher ageing temperatures were, depending on the degree of cold-working to which the alloys had been subjected, very high.

Influence of Hot Working on Creep Properties of Nickel

See abstract on p. 264.

Thermoelectric Stability of Nickel and Nickel-Alloy Thermocouple Materials at Elevated Temperatures

See abstract on p. 267.

British Specifications covering Nickel

See abstract on p. 269.

Leads for Miniature Electron Tubes: Specification

AMER. SOC. TESTING MATERIALS: 'Proposed Tentative Specification for Miniature Electron Tube Leads.'

Contained in Report of Committee F-1 on Materials for Electron Tubes and Seimiconductor Devices. *A.S.T.M. Preprint* 64, 1959, pp. 5–7.

The specification, which has been accepted by the Society for use pending adoption as Standard, covers the component materials and physical, chemical and dimensional requirements for three-piece leads for miniature electron tubes.

Stipulations as to the materials used are given below.

I. *Outer-Lead Materials*, 0·04 in. (1 mm.) in diameter.

(1) Nickel-plated mild steel containing not more than 0·08 per cent. carbon (nickel 4 wt. per cent. max.).

(2) Nickel-plated 30 or 40 per cent. conductivity copper-coated steel containing not more than 0·13 per cent. carbon (nickel 4 wt. per cent. min.).

(3) Grade A nickel as laid down in *A.S.T.M. Designation F*175.

(4) Nickel-clad copper (27–29 wt. per cent. nickel).

(5) Grade A nickel plated with 0·5–1·5, 1·5–2·5, or 3·5–4·5 wt. per cent. of silver.

(6) Grade A nickel clad with 4·5–5·5 or 8–10 wt. per cent. of silver.

II. *Seal Materials*, 0·016 in. (0·4 mm.) in diameter. Borated 'Dumet'.

III. *Inner-Lead Materials*, 0·02 in. (0·5 mm.) in diameter.

(1) Nickel-plated mild steel containing not more than 0·08 per cent. carbon (7–9 wt. per cent. nickel).

(2) Nickel-plated 30 or 40 per cent. conductivity copper-coated steel containing not more than 0·13 per cent. carbon (7–9 wt. per cent. nickel).

(3) Grade A nickel, as laid down in *A.S.T.M. Designation F*175.

Influence of Nickel on the Sintering Characteristics of Tungsten

J. VACEK: 'Factors Influencing the Sintering Characteristics of Tungsten.'

Planseeberichte f. Pulvermetallurgie, 1959, vol. 7, Apr., pp. 6–17.

Powder-metallurgical production of tungsten is carried out almost exclusively by the method proposed by COOLIDGE, involving the use of sintering temperatures in the region of 2500°C., which are achieved by passage of an electric current (see *Jnl. Amer. Inst. Electrical Engineers*, 1910, vol. 29, p. 953). The advantages of sintering at lower temperatures in a conventional furnace are obvious, but the achievement of satisfactory properties in the finished product has been found to be contingent upon the use of very high sintering temperatures. Work has therefore been directed towards determining the feasibility of modifying the sintering characteristics of tungsten (so enabling use of lower sintering temperatures) by addition of small amounts of other powder metals to the tungsten prior to sintering. The investigation now recorded related mainly to determination of the effects of nickel in this respect.

Preliminary experiments were carried out to establish the degree to which small amounts (0·1 per cent.) of addition metals (added, in the form of salts, to the tungsten trioxide prior to its being reduced to the metal powder) affected the density of tungsten compacts sintered, at 1300°C. for 1 hour, in a hydrogen atmosphere. The metals added were nickel, cobalt, iron, copper, zinc, silver, manganese, lead, tin, aluminium and magnesium.

It was found that with additions of about 0·25 per cent. of nickel or cobalt a theoretical density of about 95 per cent. was obtained. Addition of iron was somewhat less beneficial, and the presence of the other metals was without effect. Experiments involving addition of more than one metal to the tungsten demonstrated that the sintering characteristics were improved when nickel and cobalt were simultaneously present. The influence of the nickel and cobalt additions was reflected in a refinement of the grain-size of the reduced tungsten powder; the other metals investigated caused a coarsening of the grains. The metals which proved beneficial were distinguished from the others by their capacity to form solid solutions with tungsten and by the fact that their oxides were reducible in hydrogen.

The major portion of the paper is concerned with the results of experiments in which the influence of nickel additions (as reflected in the density, hardness, electrical resistivity, and transverse rupture strength of sintered specimens) was determined as a function of the conditions under which the tungsten trioxide was reduced, the compacting pressure, and time and temperature of sintering.

Service Characteristics of Various Types of Aircraft Battery

A. SAGEAU, J. COUZY and R. VEYRAC: 'Comparison of the Service Characteristics of Various Types of Aircraft Electrical Accumulator.'

Docaéro, 1959, No. 54, Jan., pp. 33–48.

Up to as recently as ten years ago selection of a suitable battery for a specific aeronautical application was a relatively simple task: the only practicable batteries available were the lead type, and it was merely a question of making an approximate estimate of consumption and choosing a battery of sufficient capacity to provide for emergency-starting and other requirements. Nowadays, however, the aeronautical engineer is confronted with a range of new batteries which differ considerably in their properties. Of particular importance in this respect are the 'Andyar' zinc/silver batteries (the positive and negative plates of which are fabricated, respectively, of silver and zinc) and the nickel/cadmium batteries developed by Société des Accumulateurs Fixes et de Traction (which incorporate a nickel-hydroxide positive plate and a cadmium-hydroxide negative plate). Both types make use of a potassium-hydroxide electrolyte. Since the batteries differ in the properties they offer, it follows that their suitability for a given application will be governed by the extent to which they satisfy

the particular service requirements. With the aim of providing the engineer with general criteria on which he might base his choice of battery, the authors review the characteristics of lead, zinc/silver and nickel/cadmium batteries in relation to the main operational variables involved in aeronautical service.

The following factors are considered:

(1) Ability to provide electrical power for supplementary and emergency services, and engine starting in flight or on the ground.

(2) Adaptation of the aircraft supply system to the voltage (28 v.). Necessity for automatic contactors and/or boosters.

(3) Behaviour under conditions of cold and heat. Ventilation.

(4) Influence of atmospheric pressure.

(5) Endurance in relation to repeated discharging and re-charging.

(6) Maintenance and storage.

(7) Weight and volume.

(8) Price of standard accumulators.

(9) Selection of type of battery in relation to type of aircraft.

In an appendix to the paper a summary is made of the salient characteristics of various nickel/cadmium and zinc/silver batteries of reduced weight and bulk.

Properties of Nickel Fluoride: Literature Survey

R. K. STEUNENBERG: 'A Review of the Unclassified Literature on Nickel Fluoride.'
U.S. Atomic Energy Commission, Report ANL-5925, Oct. 1958; 31 pp.

Interest in the properties of nickel fluoride is increasing, in view of the extensive use of nickel and high-nickel alloys for equipment handling fluorine and highly-reactive fluorides. The suitability of nickel, in this connexion, is believed to be governed by the formation of a protective surface film of nickel fluoride, and that salt is frequently present, as an impurity, in fluorides which have been in contact with such equipment. In the present report an attempt has been made to review the literature to date, and to summarize pertinent physical and chemical data.

The information presented is considered in sections relating to the preparation of nickel fluoride, the existence of higher nickel fluorides, physical properties and chemical properties (solubilities and solvation, adsorption of gases, reactions of nickel fluoride, complex compounds), and thermochemical data.

Control of Cereal Rusts by Treatment with Nickel Compounds

Stem rust, leaf rust of wheat and crown rust of oats occur annually on cereals in most of the grain-growing areas of North America. In some years the diseases reach epidemic proportions, damaging, to a varying degree, millions of acres of crops in Canada and the United States. Over the past fifty years the search for means of controlling the incidence of cereal rusts has been concerned mainly with the culture of varieties of wheat resistant to rust or with the development of suitable fungicides. The genetic approach involves many years of work, with no guarantee that the strain of wheat produced will not soon become susceptible to a modified form of the disease. The problem with respect to fungicides is not so much one of protecting the wheat from the onset of rust (several compounds have been found to be suitable for this purpose, provided that the plant is protected by frequent treatment from seedling stage to maturity) but of suppressing the disease when infection occurs. The findings of workers in this field appear, however, to offer some promise of a solution to the problem. Five recent papers of interest in this connexion are abstracted below.

H. L. KEIL, H. P. FROHLICH and J. O. VAN HOOK: 'Chemical Control of Cereal Rusts. I. Protective and Eradicative Control of Rye-Leaf Rust in the Greenhouse with Various Chemical Compounds.'
Phytopathology, 1958, vol. 48, Dec., pp. 652–5.

The paper discusses the results of greenhouse screening tests to determine (1) the protective, and (2) the eradicative, effects of 200 chemical compounds in controlling rye-leaf rust. Among the complexes tested were derivatives from zinc, copper, cadmium and nickel.

Of the compounds which showed both protective and eradicative properties, the most promising appeared to be the nickel-salt/amine complexes, which eradicated rust at concentrations not harmful to the plant itself. The results indicated that the protective capacity of these complexes is associated with both the amine and nickel parts of the molecule, and the eradicative or chemo-therapeutic activity with the nickel part.

B. PETURSON, F. R. FORSYTH and C. B. LYON: 'Chemical Control of Cereal Rusts. II. Control of Leaf Rust of Wheat with Experimental Chemicals under Field Conditions.'
Ibid., pp. 655–7.

This second report is concerned with field tests on thirteen chemical compounds selected on the basis of the results obtained in the screening tests described in Part I of the series (*see* preceding abstract). The relative fungicidal effect of the compounds was determined by spraying a field of wheat infected by leaf rust.

The performance of four of the compounds was outstanding and they appeared to possess both protective and eradicative properties: bis[*N*-(2-hydroxyethyl) dodecylbenzylamine] nickel (II) chloride; bis[*N*-(2-hydroxyethyl) dodecylmethylbenzylamine] nickel (II) chloride; bis[*N*-(2-hydroxyethyl) dodecylamine] nickel (II) chloride; and bis[*N*,*N*-di(2 hydroxyethyl)dodecylamine] nickel (II) chloride That nickel was a common constituent of all the mos

efficacious fungicides evaluated is considered to indicate that optimum fungicidal activity is associated with its presence.

H. L. KEIL, H. P. FROHLICH and C. E. GLASSICK: 'Chemical Control of Cereal Rusts. III. The Influence of Nickel Compounds on Rye-Leaf Rust in the Greenhouse.'

Ibid., pp. 690–5.

Following the satisfactory performance of the nickel-salt/amine complexes under field conditions (*see* abstract of Part II), further studies were initiated to compare, under greenhouse conditions, the fungicidal effects of these complexes with those of cheaper and more accessible organic and inorganic nickel compounds. The compounds were applied to rye plants, either before or after inoculation with leaf rust, thus providing a measure of, respectively, protective and eradicative action. The results of the tests are recorded in the present paper.

The nickel compounds tested are graded, on the basis of the protection which they conferred, in the following order: acetate = acrylate = carbonate = chloride = fluoride = fluoborate > bromide = citrate = nitrate = sulphate = sulphide > cyanide > hydroxide. In order of their effect as eradicative sprays, the same compounds are listed as follows: acetate = acrylate = bromide = chloride = fluoborate = fluoride = nitrate = sulphate = sulphide > carbonate = citrate > hydroxide > cyanide. All but the fluoborate showed little or no phytotoxicity at a concentration level of 0·5 lb. per 100 gal.

In tests simulating exposure to rain, bis[*N*-(2-hydroxyethyl) dodecylmethylbenzylamine] nickel (II) chloride and *N*-(2-hydroxyethyl) dodecylmethyl-benzylamine lost little of their excellent protective capacity. However, the nickel chloride hexahydrate had a lower protective action and this was lost by rain-spraying. The eradicative effect of the first and last of these three compounds was very good, despite exposure to 'rain,' but the second compound was essentially ineffective in this respect. To achieve protective action, a concentration of 70–140 gm. of nickel chloride hexahydrate per 100 gallons were required, but for eradicative action a concentration of 25–50 gm. per 100 gallons proved adequate.

The fleck stage (4–6 days after inoculation) appeared to be the time at which rye-leaf rust is most susceptible to eradication by spraying with nickel compounds, and this action appeared to be extremely rapid. Formulations of nickel chloride hexahydrate and 'Dithane' gave very good protective and eradicatory results, even when exposed to 'rain.' Nickel Dithane (nickel ethylene bisdithiocarbamate) exhibited both protective and eradicative properties. In preliminary trials the addition of ammonia to nickel-chloride solution appeared to improve the 'sticking' properties of the nickel.

F. R. FORSYTH and B. PETURSON: 'Chemical Control of Cereal Rusts. IV. The Influence of Nickel Compounds on Wheat, Oat and Sunflower Rusts in the Greenhouse.'

Ibid., 1959, vol. 49, Jan., pp. 1–3.

As a result of the findings in the previous tests, it was decided to compare, in the investigation now described, the activity of a nickel-salt/amine complex, bis[*N*-(2-hydroxyethyl) dodecylmethylbenzylamine] nickel (II) chloride, with the activities of the parent amine and of its constituent nickel salt. These initial experiments were followed by tests to assess the suitability of several inorganic nickel salts for use as protective and eradicative fungicides for leaf- and stem-rust of wheat, crown rust of oats, and sunflower rust.

It is concluded from the data obtained that the eradicative properties of the nickel-salt/amine complex are due entirely to its nickel content: the nickel-chloride salt successfully eradicated stem rust of wheat; the parent amine had no effect in this respect. In other tests it was found that leaf rust and stem rust of wheat could be controlled by treatment with relatively low concentrations of nickel compounds. Oat and sunflower seedlings were, however, more sensitive to phytotoxicity caused by the nickel, and, since concentrations producing the required eradicative effect approached the level toxic to these plants, control of crown rust of oats and of sunflower rust is deemed practical only by use of the low concentrations of nickel necessary for protective action. Experiments in which sprayed plants were exposed to simulated rain showed that such conditions were more deleterious to the fungicidal activity of water-soluble nickel salts that to the nickel-salt/amine complex.

F. R. FORSYTH and B. PETURSON: 'Control of Leaf Rust of Wheat with Inorganic Nickel.'

Plant Disease Reporter, 1959, vol. 43, Jan. 15, pp. 5–8.

Details are given of field tests to determine the suitability of inorganic salts of nickel for use in controlling leaf rust. The authors are convinced that these compounds, particularly nickel chloride and nickel nitrate, can be used to control leaf rust, and presumably also stem rust, of wheat in the field. Increases in yield ranging from 8 to 21 per cent. were achieved. Concentrations of about 1 lb. per acre produced optimum results, and it is recommended that spraying should be effected at intervals of 7–8 days during the period after the onset of rust.

Titration of Nickel Acetate in Glacial Acetic Acid

A. T. CASEY and K. STARKE: 'Acidimetric Titration of Metal Acetates in Glacial Acetic Acid.'

Analytical Chemistry, 1959, vol. 31, June, pp. 1060–2.

Reactions in glacial acetic acid have been extensively studied in recent years, and interest has been aroused in the uses of the solvent in analytical chemistry. The investigation described was carried out to obtain further information on the estimation of metals by titration in glacial acetic acid.

Attempts were made to titrate salts of the following elements: sodium, potassium, ammonium, lithium, magnesium, calcium, barium, strontium, zinc, cadmium, manganese, cobalt, nickel, silver, lead, iron, chromium, aluminium, copper, tin, antimony, bismuth, uranium. Salts of the first eighteen metals were successfully titrated. Most of the metals were easily dissolved as acetates, or alternatively, as nitrates (the nitrate radical was then decomposed with acetic anhydride). A solution of 3 milli-equivalents of the salt in 40 ml. of acetic acid proved a convenient solution for titration. No satisfactory end-point could be obtained when titrating acetates of chromium and nickel with perchloric acid in acetic acid. Reproducible but poorly defined end-points were, however, obtained by using a solution of perchloric acid in dioxane. The acetates of aluminium, chromium, and iron gave anomalous results, while those of copper, tin, antimony, bismuth and uranium behaved as if they were unassociated in acetic acid, and could not be titrated.

Data from the titrations were used to calculate the percentage purity of the metal acetates.

The accuracy of the technique is shown to be comparable to that obtained by conventional analytical methods.

Photometric Determination of Nickel in Copper-Nickel Alloys

M. C. STEELE and L. J. ENGLAND: 'Photometric Determination of Nickel in Copper-Nickel Alloys.'
Analytica Chimica Acta, 1959, vol. 20, June, pp. 555–8.

Nickel is determined in the presence of copper by absorptiometric measurements of nickel-nitrate solutions at a wavelength of 3900 Å. The method described has been applied, using precision photometric techniques, to determination of nickel in copper-nickel alloys containing from 1 to 32 per cent. of the metal. A single determination can be completed in less than 5 minutes.

The following procedure is used: The alloy (1000 gm.) is dissolved in 10 ml. of nitric acid (specific gravity 1·4) contained in a 100-ml. beaker, and boiled to remove nitrous fumes. (Boiling is necessary because nitrites interfere.) The beaker is removed from the hot plate, allowed to cool to about 80°C., and 10 ml. of phosphoric acid (1 : 10) is then added. (Manganese as permanganate will interfere if phosphoric acid is added before boiling ceases.) The solution is cooled, diluted to 25 ml. in a volumetric flask, and, if turbid, filtered through a double No. 40 paper. (Tin as metastannic acid, silicon as silica, and carbon, if present, will interfere.) Finally, the transmittance is measured at 3900Å against a reference solution about 1 per cent. below the expected nickel content.

Determination of Nickel in Stainless Steels by Fluorescent X-Ray Analysis

See abstract on p. 276.

Determination of Nickel by Extraction with Coloured Cations

(I) L. DUCRET: 'Mineral-Analysis Determinations by Extraction with Coloured Cations. I. Introduction.' *Analytica Chimica Acta*, 1959, vol. 20, June, pp. 565-7.

(II) L. DUCRET and L. PATEAU: 'Mineral Analysis Determinations by Extraction with Coloured Cations. II. Use of *o*-Phenanthroline Complexes for the Separation and Determination of Small Amounts of Nickel in the Presence of Iron and Cobalt.' *Ibid.*, pp. 568–72.

In Part I the author discusses the feasibility of using organic cations in an extraction technique for spectrophotometric determination of simple and complex anions. Two types of coloured cations are considered suitable for this purpose: *o*-phenanthroline derivatives, and cations of basic dyes. The method discussed is stated to be particularly applicable to determination of trace elements.

In Part II an extraction method involving the use of *o*-phenanthroline as complexing agent is illustrated in relation to the separation of nickel from iron and cobalt, and determination of the nickel. The technique, although somewhat less accurate than the classic gravimetric procedure using dimethylglyoxime, can be carried out very rapidly.

ELECTRODEPOSITION AND OTHER COATING METHODS

The History of Nickel Plating

G. DUBPERNELL: 'The Story of Nickel Plating.'
Plating, 1959, vol. 46, June, pp. 599–616.

The first commercial nickel-plating process introduced in the United States was that based on a nickel-ammonium-sulphate solution, evolved by Isaac Adams over 90 years ago. This article, which is based on a *bibliography* of 203 items, represents a concise but comprehensive historical survey of the main developments in nickel plating since that time.

A 'potted' biography of Adams is used by the author as a background against which to outline, in some detail, the pioneer work of the early investigators. Discussion of the early patent literature includes references to a claim, taken out by Weston in 1878, covering the use of boric acid in plating solutions. Since that date a considerable amount of research has been carried out on methods of determining the content of the acid in plating solutions, and reference is made to the main features of this work.

An outline is given of the investigations preceding and following the discovery of the beneficial effects, on anode dissolution, of chloride additions to the electrolyte. A short review of the literature relating to the use of weakly acidic plating solutions, and to the introduction of pH measurements as a means of controlling the solution, is followed by a more extensive section describing the events and work which finally culminated in the development,

by O. P. Watts, of his well-known nickel-plating solution. Attention is then directed to the literature on fluoborate and sulphamate solutions, and an account is given of the research and personalities involved in the development of bright-nickel plating. The latter section is supplemented by a list of the more important primary and secondary brighteners, and the United States and Canadian patents covering their use. The author ends his survey with a discussion of estimates, compiled from various sources, of the amounts of nickel used annually for electroplating.

Electrodeposition of Nickel from the Pyrophosphate Solution

S. K. PANIKKAR and T. L. R. CHAR: 'Electroplating of Nickel from the Pyrophosphate Bath.'

Jnl. Electrochemical Soc., 1959, vol. 106, June, pp. 494–9.

The report is one of a series describing experiments carried out to study the electrodeposition of various metals from pyrophosphate solutions (see references to previous papers by CHAR in *Nickel Bulletin*, 1958, vol. 31). The present paper records the results of a comprehensive investigation of the plating variables involved in electrodeposition of nickel.

The nickel concentration was varied between 0·05 and 0·8 M, the ratio of pyrophosphate to metal between 6 and 10, and the pH between 7·8 and 10·5. The solution was operated at temperatures of 30°, 50°, 60° or 70°C.

The results, which are presented in terms of the nature of the deposit, current efficiencies, potentials, throwing power, and stability of the solution, demonstrate that nickel coatings of good quality can be deposited from the pyrophosphate solution over a wide range of operating conditions. The authors compare the plating characteristics of Watts and chloride nickel-plating solutions with those exhibited by the pyrophosphate bath and conclude that the latter is equivalent in all essential features to the acid solutions. It offers, moreover, the following advantages: low metal content, high throwing power, and ability to plate directly onto zinc.

Thickness of Nickel Electrodeposits

'How Much is Enough ?'

Metal Finishing Jnl., 1959, vol. 5, June, p. 221.

This leader was written in the light of the decision taken by the American Society for Testing Materials Committee on Electrodeposited Metallic Coatings to double the thickness of nickel stipulated in the specification for electrodeposited coatings of nickel and chromium on zinc and zinc-base die-castings (see abstract in *Nickel Bulletin*, 1959, vol. 32, No. 7, pp. 213–14). The writer makes the following comments:

'The fact that no move was made to introduce the new specification until nickel was in abundant supply may be taken as a tacit implication that the earlier specification was dictated more by considerations of maintaining production than by a desire to ensure adequate performance of the coating. This is an attitude which has been far too long apparent on the metal-finishing scene, and the amount of harm which it has done to the electroplating industry must be considerable. Complaints concerning the performance of plated coatings, particularly on zinc-alloy die-castings, have been legion in the post-war years and have lent considerable impetus to the quest for alternative finishes and materials. The argument has been put forward that it is better to have inadequately plated components than no component at all, and the stringency of the nickel shortage was such that all too often such a choice had to be made. One can still remember the effort that was put into discovering methods of replacing the missing nickel as an undercoat to chromium, both by established research bodies and by extempore organizations. That these were largely unsuccessful is a measure of the importance of the rôle played by nickel, which in its turn makes it all the more essential that these earlier inadequacies should be urgently adjusted now that the shortage is ended.'

The reputation of nickel/chromium plating will, in the writer's opinion, be maintained only by specification of a nickel coating of sufficient thickness to preclude any possibility of premature failure, and thereafter, by rigid inspection, ensuring that the specified thickness of nickel is deposited on all significant areas of every component.

Corrosion-Resistance of Duplex Nickel Coatings

'Duplex-Type Nickel Plate Protects Zinc Die-Castings.'

Iron Age, 1959, vol. 183, June 11, pp. 132–3.

The article is based on a report, by M. R. CALDWELL, of investigations carried out by Doehler-Jarvis Division of National Lead Company, Toledo, with the aim of improving the corrosion-resistance of nickel/chromium coatings deposited on zinc die-castings. Three methods of achieving this aim were initially considered: production of a crack-free chromium overcoating, increasing the thickness of the nickel coating, use of a duplex nickel deposit. Development work was finally concentrated on the last approach to the problem.

The duplex coatings tested consisted of an underlayer of semi-bright nickel (deposited over a copper flash and representing about 60–75 per cent. of the total nickel thickness) and a second layer of bright nickel. The semi-bright layer, which has a columnar structure, is deposited from a solution containing no sulphur-bearing organic compounds. A typical nickel/chromium coating produced by the Doehler-Jarvis Division would comprise copper 0·0004 in. (0·01 mm.), nickel 0·0008 in. (0·02 mm.), chromium 0·00001 in. (0·00025 mm.).

The corrosion-resistance of duplex coatings is stated to be from 25 to 33 per cent. higher than that of conventional bright-nickel deposits. Photomicrographs included in the article show that corrosive attack is so retarded by the semi-bright layer that

corrosion proceeds laterally, instead of penetrating vertically through the deposit to the basis metal.

The results of comparative corrosion tests (atmospheric, 'Corrodekote' and accelerated acetic-acid/salt-spray) on bright-nickel and duplex-nickel coatings are summarized in diagrammatic form. In all cases the duplex coatings exhibited superior corrosion-resistance. In further tests, run by an automobile company, duplex and bright-nickel coatings were exposed to: the acetic-acid/salt-spray test (8 days); the neutral salt-spray test (8 days); the copper-accelerated acetic-acid/salt-spray test (16 hours and 48 hours); and to the atmosphere (for 34 days). Whereas the duplex coatings showed no signs of corrosion (except in the neutral salt-spray test, in which both types of coating were seriously attacked), the bright-nickel deposits were corroded in spots through to the base metal.

See also

'Improvements in Plating Zinc Die-Castings.'
Metal Progress, 1959, vol. 75, June, pp. 78–81.

Deposition of Nickel by Thermal Decomposition of Nickel Carbonyl

L. W. OWEN: 'Observations on the Process of Nickel Deposition by Thermal Decomposition of Nickel Carbonyl at Low Pressures.'
Metallurgia, 1959, vol. 59, Apr., pp. 165–73; May, pp. 227–33; June, pp. 295–301.

Although in recent years much interest has been aroused by plating techniques involving deposition of a metal by thermal decomposition of a suitable metallic compound (e.g., a carbonyl or halide), the relevant literature is by no means comprehensive. Deposition of nickel at low pressures viâ thermal decomposition of the carbonyl, the technique which appeared to offer most promise of yielding acceptable coatings, was selected for study in the investigation described by the author.

The properties of nickel carbonyl and decomposition of the vapour have been the subjects of fairly extensive study (references are given to the literature), but the mechanism of deposition and the properties of the nickel coatings obtained have received little attention, and little guidance is available on the equipment used. The author has consequently thought it necessary 'to record observations, experiences and results of experimental determinations in more detail than might otherwise be usual in a paper such as this, and it is hoped that the information will be both useful as an introduction to more detailed studies, and as a guide to the procedure and practice to be adopted for the operation of the process'.

Most of the specimens used for the plating tests were flattened cylinders 0·5 in. (1·25 cm.) in length and 1 in. (2·5 cm.) in diameter; a few larger cylinders were, however, employed in tests for porosity. Only a brief account is given of the plating unit employed, since a detailed description was given by the author in *Metal Industry*, 1958, vol. 92, Mar. 21, pp. 227–30.

After degreasing and a light etching treatment the specimens were transferred to the plating unit, and held at 400°C. for one hour at 0·1 μ, to remove gases adsorbed at the surface. Some specimens were given additional pre-treatments to promote adhesion of the coating. In general, plating was carried out under the following conditions:

Temperature: 200°C.
Pressure in the plating vessel: 1–2 mm.
Rate of flow of carbonyl vapour equivalent to 1–1·5 g. of nickel per hour.
Direction of vapour flow: downward.

The findings of investigations concerned with the variables governing deposition of the nickel, and with the properties of the coatings obtained, are outlined by the author in sections referred to below:

I. *Main Variables Influencing the Deposition Process.*
   1. Temperature of the specimen.
   2. Rate of flow of the nickel-carbonyl vapour.
   3. Pressure and linear velocity of the vapour.
   4. Composition of the plating gas.
      (Experiments were made to determine the effects of diluting the nickel-carbonyl vapour with carbon monoxide, hydrogen, argon, nitrogen or oxygen.)
   5. Size of the specimen and of the bell jar used as the plating vessel.

II. *Distribution of Coating Thickness on Specimens of Simple Shape.*

III. *Ability to Deposit Coatings of Desired Average Thickness.*

IV. *Adhesion of the Coatings to Various Metallic Bases.*
   (Coatings were produced on aluminium, brass, copper, lead, magnesium, mild steel and zinc.)

V. *Porosity of the Coatings.*

VI. *Physical and Mechanical Properties of the Nickel Coatings.*
   1. Appearance.
   2. Microstructure (the paper includes photomicrographs illustrating the various structures exhibited by the coatings).
   3. Hardness.
   4. Ductility.

The findings are correlated and discussed *in extenso* in the final part of the paper. The author summarizes his conclusions as follows:

'Coatings of good appearance and properties have been obtained readily by this method of deposition, at a high efficiency of vapour decomposition. Control of temperature was the most important factor as regards the soundness of the coating, whilst accurate control of vapour flow was important in applying a desired weight of coating.

'A high degree of adhesion of the coating is necessary on certain metals, vacuum outgassing and post-deposition heat-treatment being beneficial for achieving this. Except in the thinnest coatings, porosity was generally of a low order. Distribution of coating thickness over solid objects and into recesses was generally good, and could be improved by reversing the direction of vapour flow and by special devices.

'Within the range of conditions studied, defective as well as sound coatings were obtained, and, in the range of sound coatings, there was a good deal of variation between just acceptable and extremely good quality. The basis of assessment was mainly ductility. Bend-test values from less than one bend through 90° to as much as 20 bends through 180° were obtained.

'Appearance, ductility, micro-hardness and structure varied considerably and often unaccountably. Bright coatings with medium-size compact grains were frequently the most ductile. Brittleness was most frequently found in matt coatings with fissures or loose grains or oxide structures; coatings with large grains usually had low hardness values; those with small or with microscopically invisible grains had high hardness values and low ductility. Dendritic, fine-grained, and fibrous types of structure were most frequently obtained. All deposits except those heavily oxidized during plating underwent re-crystallization on heat-treatment, to give a polygonal equi-axial type of grain. Temperature was the most critical of the variables. Deposition at temperatures below 200°C. was accompanied by specific defects in the coating: darkness in colour and a velvety or powdery appearance, brittle fissured dendritic type of structure, and low deposition efficiency. As the temperature was increased from 200°C. up to about 230°C., depending upon conditions (size and geometry of specimen and bell jar, rate of flow, pressure, etc.), the deposit improved in appearance and properties. At about 250°C. black powdery deposits formed on the bell jar and in the vicinity of the specimen. The optimum plating temperature was probably the maximum that could be used without black-powder formation, but not less than 210°C. and, for best thickness distribution of coating, possibly not more than 230°C.

'Rate of flow of nickel-carbonyl vapour and pressure did not appear to be critical factors, although they have not been investigated independently of one another. High rates of flow, and pressures much above 2-3 mm., seemed to result in coatings of less satisfactory appearance and increased tendency to black powdery decomposition of the carbonyl vapour, but it was nevertheless an outstanding feature of this process that plating rates of up to 20×10^{-3} in. per hour could be employed without drastic deterioration of coating properties. Conditions where particle formation in the vapour phase is of a low order would appear desirable for coatings of the best quality. It is not possible to say how these conditions can be determined, but low pressures, high linear velocities of vapour, and additions of carbon monoxide are probably favourable factors. The direction of vapour flow, i.e., upward or downward, affected the distribution of coating thickness. Diluent gases did not appear to exert marked beneficial effects, with the exception of carbon monoxide, which inhibited black-powder formations and resulted, in certain conditions, in improved coatings. Oxygen in the nickel-carbonyl vapour profoundly affected the properties of the coating, extreme brittleness, drastic increases in hardness, and a characteristic banded type of micro-structure being observed.'

Applications of Nickel in the Vehicle Industry

See abstract on p. 258.

Cadmium Plating of Stainless and High-Strength Constructional Steels

See abstracts on pp. 273 and 259.

NON-FERROUS ALLOYS

Diffusion of Iron in Nickel-base Alloys

A. Y. SHINYAER: 'Diffusion in Nickel-base Limited Solid Solutions.'

Fiz. Metall. i. Metalloved., 1958, vol. 6, pp. 450-5.

Report of determination of the diffusion coefficients of iron in the following alloys: nickel-titanium (8 per cent. Ti by wt.); nickel-titanium-chromium (3·4% Ti, 20% Cr), and nickel-titanium-chromium-tungsten-aluminium (3% Ti, 20% Cr, 6% W, 4½-5% Al). Small discs were coated with radioactive Fe^{59} on one side and were heated at temperatures within the range 950°-1250°C. for various times. The specific activities of the different layers were determined, and diffusion coefficients were calculated. For brief summary of results, see *Chemical Abstracts*, 1959, vol. 53, Apr. 25, p. 6969.

Precipitation from Solid Solution: Educational Lectures

See abstract on p. 245.

Production of Nickel Silver Wire for Spectacle Frames

'Large-Quantity Production of Spectacle-Frame Reinforcing Wires.'

Machinery (*Lond.*), 1959, vol. 94, May 20, pp.1146-9.

Among the products manufactured by Change Wares, Ltd., Morden, Surrey, are reinforcing wires for spectacle frames (i.e., the small-diameter wire inserted into each leg of the frame to stiffen the plastic material, while permitting a certain degree of controlled flexibility). The wires, which are made from nickel silver, vary in size according to requirements, but, irrespective of type, they are characterized by three basic manufacturing stages: the wire, supplied in coil form, is straightened and cut to length, one end is then ground to a sharp point, and finally the other end is flattened for a distance of about one-third to one-quarter of the total length. Since any surface imperfections are greatly magnified

when the wire is embodied in the plastics material a high finish is essential; the flattened part in particular is required to have a mirror finish.

The technique developed is such that after completion of the flattening operation no further polishing or finishing process is necessary. This article gives details of the machinery and procedure used.

Influence of Cold-Drawing and Annealing on the Modulus of Rigidity of 'Monel', and 'CA Alloy'

See abstract on p. 246.

Thermoelectric Stability of Nickel-Alloy Thermocouple Materials at Elevated Temperatures

See abstract on p. 267.

British Specifications covering High-Nickel Alloys

See abstract on p. 269.

Machinable High-Density Tungsten-Nickel-Copper Alloys: Specification

AMER. SOC. TESTING MATERIALS: 'Proposed Tentative Specification for Machinable High-Density Tungsten-Nickel-Copper Alloys.'

Contained in Report of Committee B-9 on Metal Powders and Metal-Powder Products.
A.S.T.M. Preprint 15, 1959, pp. 6–7.

The specification lays down requirements with respect to the composition, density, hardness, tensile properties and machinability of powder-metallurgically-produced alloys of the following composition: tungsten 90±1, nickel 6±2, other elements 1·5 max., per cent., remainder copper.

Minimum densities of 16·8, 16·7 and 16·5 gm./cm.^{3} are stipulated for parts of, respectively, less than 500, 500 to 2,500, and greater than 2,500 gm. in weight.

Photometric Determination of Nickel in Copper-Nickel Alloys

See abstract on p. 250.

NICKEL-IRON ALLOYS

Use of Nickel-Iron Films in 'Memories' of Digital Computers

E. E. BITTMANN: 'Using Thin Films in High-Speed Memories.'

Electronics, 1959, vol. 32, June 5, pp. 55–7.

Although the performance of ferrite cores in memories for digital computers is excellent, such memories are difficult to assemble, and the method of threading each ferrite core with one or more conductors is costly and does not lend itself to automation. Thin films operate in the millimicro-second range, and over a much wider range of temperature than ferrites. Fabrication of ferro-magnetic thin-film memories is relatively simple, and automatic assembly is feasible: experimental results indicate that complete memories can be made by deposition, onto a substrate, of magnetic materials and conductors.

The main features of a high-speed memory which makes use of a nickel-iron-alloy film are outlined in this article, in sections concerned with vacuum-deposition and behaviour of the film, the memory array, storage of an information bit, fabrication of the memory, and circuits.

Magnetic Tape produced by Powder Metallurgy

C. E. RICHARDS: 'British Achievements with Magnetic Tape Rolled from Powdered Metals.'

Reprint from *Electrical Manufacturing*, 1957, vol. 9, Dec., pp. 104–8.

HENRY WIGGIN AND CO., LTD., *Publn.* 1565*, 1959; 15 pp.

See abstract in *Nickel Bulletin*, 1958, vol. 31, No. 5, p. 135.

CAST IRON

Vibration of Nickel-containing Iron and Steel Castings during Solidification

J. H. GITTUS: 'The Inoculation of Solidifying Iron and Steel Castings by means of Vibration.'

Jnl. Iron and Steel Inst., 1959, vol. 192, June, pp. 118–31.

Previous investigations concerned with the effects of vibrating molten or solidifying metals have shown that such treatment can result in grain refinement, degasification, and the emulsification of immiscible phases. Work in this field has been carried out mainly on non-ferrous alloys, and relatively little on steels. The only published report for cast iron is that by RICHARDS and ROSTOKER, who found that the size of the graphite flakes in an iron casting could be increased by vibration (see *Trans. Amer. Soc. Metals*, 1956, vol. 48, pp. 884–903). The investigation now described was carried out to obtain further information on the influence of vibration on iron and steel castings.

Most of the iron castings studied were produced from metal having a residual magnesium content (obtained by treatment with nickel-magnesium alloy) of the order employed for the production of spheroidal graphite. Two steels were selected for study: one of low-alloy nickel-chromium-molybdenum type (equivalent to a B.S. En 24 grade), the other an unalloyed steel with a 1·4 per cent. carbon content. The iron and both steels were cast, through a top feeder, into the form of spheres 2¼-in. (5·5-cm.) in diameter, the iron at a pouring temperature

* We shall be pleased to supply a free copy of this publication.

of 1400°C., the steel at 1540°C. The moulds were either machined from graphite electrodes or rammed-up in silica sand bonded by the CO_2/sodium-silicate process. Comparison of the results obtained using these two moulding materials made possible an appraisal of the effects of solidification rate. During solidification the castings were vibrated, by means of a mains-energized solenoid, at 100 c/s with maximum amplitude of about 0·05 in., and some of the iron castings, after examination in the as-cast condition, were subjected to an annealing treatment.

In the experiments with cast iron particular attention was paid to the effects of varying the amplitude of vibration, and to the relative and cumulative effects of vibration and of ladle inoculation.

The analytical and hardness data presented in the paper are supplemented by numerous photomicrographs illustrating the microstructural effects of vibration. The author's summary of the findings is quoted below:

'The conventional columnar structure of the austenite dendrites in steel and the primary carbides in hypereutectic white iron are largely eliminated by vibration. The former are replaced by equiaxed dendrites, the latter by carbide platelets of random orientation.

'Magnesium-treated cast iron, which would normally be substantially carbidic, can be graphitized by vibration to give spheroidal graphite, even when the silicon content is less than 0·2 per cent. and the metal is cast into a chill mould.

'Vibration, during solidification, of a chill-cast En 24-type steel markedly reduced micro-segregation, but produced a thin band of macro-segregation some distance from the cast surface. The position of this band varied with the rate of solidification. By casting into a vibrating sand mould instead of a chill mould, the solidification rate was reduced and the segregated band was eliminated.'

A theory is proposed to explain the general phenomenon of inoculation in iron castings.

Austenitic Nickel-Chromium-(Copper) Grey-Iron Castings: Specification

AMER. SOC. TESTING MATERIALS: 'Proposed Tentative Specification for Austenitic Gray Iron Castings.' Contained in Report of Committee A-3 on Cast Iron.

A.S.T.M. Preprint 2, 1959, pp. 4–8.

The specification covers requirements with respect to manufacture (melting and heat-treatment), composition, mechanical and magnetic properties, and testing of austenitic heat-, corrosion- and wear-resisting grey-iron castings. Six grades of iron are considered, the compositions and mechanical properties for which are given in the table below. Test specimens and testing conditions are laid down for evaluation of both magnetic and mechanical properties.

A.S.T.M. Specification for Austenitic Cast Irons

Type	Composition								Mechanical Properties	
	C %	Si %	Mn %	Ni %	Cu %	Cr %	S %	Mo %	Tensile Strength min.	Brinell Hardness (3000 kg.)
Type 1 (*a*)	3·00 max.	1·00-2·80	1·00-1·50	13·50-17·50	5·50-7·50	1·75-2·50	0·12 max.		25,000 p.s.i. (11·15 t.s.i.) (17·6 kg./mm.²)	131-183
Type 2 (*a*) (*b*)	3·00 max.	1·00-2·80	0·80-1·50	18·00-22·00	0·50 max.	1·75-2·50	0·12 max.			118-174
Type 3	2·60 max.	1·00-2·00	0·40-0·80	28·00-32·00	0·50 max.	2·50-3·50	0·12 max.			118-159
Type 4	2·60 max.	5·00-6·00	0·40-0·80	29·00-32·00	0·50 max.	4·50-5·50	0·12 max.			149-212
Type 6	3·00 max.	1·50-2·50	0·80-1·50	18·00-22·00	3·50-5·50	1·00-2·00	0·12 max.	1·00 max.		124-174
Type 5	2·40 max.	1·00-2·00	0·40-0·80	34·00-36·00	0·50 max.	0·10 max.	0·12 max.		20,000 p.s.i. (8·9 t.s.i.) (14 kg./mm.²)	99-124

(*a*) By agreement between the purchaser and the manufacturer, the chromium content of Types 1 and 2 may be 2·50-3·50 per cent. for special service involving erosion-resistance. These grades shall be designated as Types 1a and 2a.

(*b*) In the same manner, for special heat-resisting service the chromium content of Type 2 may be 3·00-6·00 per cent. and the grade shall be designated as Type 2b.

For Types 1a, 2a and 2b, a minimum tensile strength of 30,000 p.s.i. (13·4 t.s.i.; 21·1 kg./mm.²) is specified. Brinell hardness range for Type 1a is 149-212, and for Types 2a and 2b 149-248.

CONSTRUCTIONAL STEELS

Influence of Composition and Processing Variables on the Mechanical Properties of Rotor Forgings

K. H. KRAMER and J. E. STEINER: 'Effect of Composition and Processing Variables on some Mechanical Properties of Large Nickel-Molybdenum-Vanadium Rotor Forgings.'

Amer. Soc. Testing Materials, 1959, *Preprint* 76; 6 pp.

Investigation of certain failures of large turbine and generator rotor shafts which have occurred in the U.S.A. has shown that, in practically every instance, the steel failed in a brittle manner and that the impact-transition temperatures of the steel fragments were high. As one approach to obtaining improved notch-toughness in rotor forgings, several producers and users have employed statistical methods to determine the coefficients in equations relating the V-notch Charpy fracture-appearance transition temperatures of large nickel-molybdenum-vanadium-steel forgings to composition and processing variables. The present paper describes one such approach, in which a regression analysis was carried out. Equations relating tensile strength and yield strength to composition and processing variables are also outlined.

The multiple regression analysis indicated that the fracture-transition temperature rises with rise in austenitizing temperature and with increase in carbon, manganese, molybdenum, and phosphorus contents and falls with increase in nickel content and rise in tempering temperature. Tensile strength and yield strength increase with increases in carbon, nickel, chromium and molybdenum contents and decrease with rise in tempering temperature. These results are expressed quantitively in the form of equations. The most important conclusion drawn by the authors is that both impact and tensile properties of large nickel-molybdenum-vanadium-steel forgings should be improved by increasing the nickel content of the steel.

Influence of Prior Stress Cycling on Mechanical Properties of Nickel-Chromium-Molybdenum Steels

J. MARIN, P. BORACHIA and U. A. RIMROTT: 'The Effect of Stress Cycling on the Static Mechanical Properties of SAE 4340 Steel.'

Amer. Soc. Testing Materials, 1959, *Preprint* 68; 12 pp.

A search of the literature had shown that the effects of prior stress cycling have been studied mainly in relation to the dynamic properties of materials, and little or no work has been carried out to determine the influence of pre-cycling on static properties. In the investigation now recorded specimens of low-alloy nickel-chromium-molybdenum steel (A.I.S.I. 4340 grade), heat-treated to a nominal ultimate strength of about 140,000 p.s.i. (62·5 t.s.i.; 98·5 kg./mm.^{2}) were pre-cycled, under axial tensile loading, to various percentages of the fatigue life for the specific stress level selected. Tensile tests were then conducted, and from the stress/strain curves so obtained the static mechanical properties of the steel were determined and compared with those of control specimens which had not been subjected to prior pre-stressing.

The general conclusion drawn from the results of these tests is that pre-cycling has relatively little effect on the static properties of the steels. All the pre-stressed conditions, with the exception of those involving pre-cycling at $\pm$70,000 p.s.i. (31·2 t.s.i.; 49·2 kg./mm.^{2}) to 70 per cent. of the fatigue life were found slightly to reduce the hardness. In most cases pre-cycling slightly increased both the true and nominal ultimate strength and decreased the nominal ductility (as determined by reduction in area). A large increase in strain hardening resulted from pre-cycling, the average increase being 13·7 per cent.

Various theories have been proposed to explain the mechanism of fatigue, some of which are based on the concept that materials have a certain available ductility, and that, under stress-cycling conditions, failure will occur when the resultant permanent strain or ductility has reached the fracture strain under static loading. This interpretation of fatigue failure in terms of depleted ductility is not supported by the results of the investigation.

Vibration of Steel Castings during Solidification

See abstract on p. 254.

Spreading of Nickel-containing Steels during Rolling

W. GROSSE and H. GOTTWALD: 'The Influence of Carbon, Manganese, Chromium, Nickel and Molybdenum on the Free-Spreading of Steels.'

Stahl u. Eisen, 1959, vol. 79, June 11, pp. 855–66.

The investigation described was carried out to throw light on the factors involved in the lateral flow of steels during rolling.

Tests were made on slabs of the same grade of steel, 70-mm. thick, but varying in width. Into each slab were incorporated, perpendicularly, and in some cases horizontally, to the rolling direction, wire rods, the changes in the position and thickness of which, after the slabs had been rolled to a thickness of 40-mm., reflected the material flow over the cross-section of the slab. The results illustrate the decisive influence, in this connexion, of the initial cross-section of the slab, i.e., the ratio of thickness to width.

Further experiments were designed to determine the influence, on the lateral spread of the steels, of composition and rolling temperature. The rolling temperatures used were in the range 900°–1150°C., and the effects of alloying additions of carbon, manganese, nickel, chromium and molybdenum were

established by rolling tests on carbon, high- and low-manganese, high- and low-chromium, low-alloy nickel-chromium, 18-8 type chromium-nickel, and chromium-molybdenum steels.

The results are presented *in extenso*. Details are given of a factor which, derived from the curves obtained, permits assessment of the spreading characteristics of the individual steels.

Crack Propagation in High-Strength Steel Sheet

J. E. SRAWLEY and C. D. BEACHEM: 'Crack-Propagation Tests of Some High-Strength Sheet Steels.'

U.S. Naval Research Laboratory, Report 5263, Jan. 10, 1959; 26 pp.

In an earlier report by the authors it was shown that a convenient empirical comparison of the crack-propagation characteristics of high-strength sheet materials could be obtained by tensile tests on specimens (as little as ½ in. (1·25 cm.) in width) into which had been introduced transverse cracks of controlled size located in the centre of the specimens and extending through their thickness. (See *Naval Research Laboratory, Report* 5127, Apr. 9, 1958.) Data presented in that report related only to two hardenable 12 per cent. chromium steels, but the test programme has since been extended to cover not only these two materials, but also a range of other high-strength steels. The purpose of the present report is to record the results to date and to describe the modified specimens and equipment used.

Four grades of steel were investigated: the two martensitic stainless steels previously studied; three martensitic low-alloy steels (nickel-chromium-molybdenum-vanadium, chromium-molybdenum-vanadium, and chromium-molybdenum); two hot-work die steels; and a precipitation-hardenable stainless steel containing chromium 17, nickel 7·2, aluminium 1·15, per cent. Conventional and slotted tensile specimens of each steel were subjected to the same heat-treatment, and the slotted specimens were then cracked, at each end of the slot, by hydrogen embrittlement and straining (i.e., by cathodic charging in dilute sulphuric acid and by straining at a stress about equal to one-third of the yield strength of the material). Finally, before testing, the slotted test pieces were baked to remove hydrogen, and the control specimens were similarly treated. In most cases the heat-treatments used were those recommended by the manufacturer.

In the report the net fracture stress and fracture appearance (in terms of the percentage of the thickness of the specimen occupied by the shear borders) are presented as a function of the test temperature, over a range sufficiently wide to include the transition from brittle to tough behaviour. The conventional ultimate and yield strengths are also given over the same range.

The fracture-appearance transition temperature is defined as the lowest temperature at which a specimen would exhibit an entirely shear fracture, and the net fracture-stress transition temperature is arbitrarily defined as the lowest temperature at which the net fracture stress would equal the yield strength. As a tentative criterion for evaluation of the materials, it is suggested that, if the risk of brittle failure is to be minimized, the fracture-appearance transition temperature should not exceed the lowest operational temperature. The advantage of the fracture-appearance criterion is that it is one which can usually be readily applied to all types of test and service failures.

The process of fracturing for the type of specimen used and its relationship to the value of the net fracture stress are discussed, and some information is presented on the influence of heat-treatment for a given steel in a given thickness, and on the influence of thickness for a given steel in a given condition. For some of the steels, too low a width-to-thickness ratio (about 5 or less) will result in unreliable net fracture-stress values above the transition temperature, indicating that the material should be re-tested, using wider specimens.

Of the steels tested, only two were found to combine a room-temperature yield strength of more than 200 kg./sq. in. with fracture-appearance transition temperatures at or below room temperature. One was the nickel-chromium-molybdenum-vanadium low-alloy steel (0·083 in. (2·07 mm.) thick), the other the semi-austenitic precipitation-hardening steel (0·1 in. (2·5 mm.) thick). Further testing of these two steels is recommended. The net fracture-stress values exhibited by specimens cracked by hydrogen embrittlement and straining showed good agreement with those obtained from tests on specimens cracked by fatigue stressing.

Temper-Embrittlement of Low-Alloy Nickel-Chromium Steel

W. P. CLANCY and M. R. NORTON: 'Microstructural Observations Pertinent to the Tempering and Temper Brittleness of Steel.'

Proc. Amer. Soc. Testing Materials, 1958, vol. 58, pp. 912-30; disc., p. 931.

WOODFINE has suggested that the increase in Charpy impact-transition temperature associated with increase in time at tempering temperatures immediately below the lower critical temperature is caused by an increase in ferrite grain-size, and has offered this suggestion as a probable explanation of so-called 'upper-nose temper-embrittlement' in alloy steels. However, data obtained by JAFFE and BUFFUM on a low-alloy nickel-chromium steel of A.I.S.I. 3140 grade gave no evidence of grain-growth (see abstract in *Nickel Bulletin*, 1957, vol. 30, No. 4, p. 59). The investigation described was undertaken by the authors on the assumption that metallographic verification of ferrite grain-growth during the tempering of a steel of similar type to that studied by Jaffe and Buffum would provide fundamental information on (1) the tempering process, and (2) upper-nose embrittlement.

Specimens of the A.I.S.I. 3140 steel (carbon 0·38-0·43, nickel 1·1-1·4, chromium 0·55-0·75, per cent.) were austenitized for one hour at 900°C.,

tempered for various times at 650°, 675° and 700°C., water-quenched, and then subjected to metallographic examination. Ferrite grain-sizes were estimated by an intercept method.

Etching studies were conducted on the A.I.S.I. 3140 steel and on carbon, nickel, manganese-vanadium, manganese-nickel-chromium-molybdenum, nickel-chromium-molybdenum, and nickel-chromium steels. The tempered specimens were etched for three to four minutes in a 0·5 per cent. aqueous solution of picric acid. To gain further information on etching effects, specimens were immersed for various times, either in the latter solution or in a reagent containing ethereal picric acid and Zephiran chloride. With the exception of the carbon steel, which was treated to produce patches of martensite in a ferritic matrix, all the materials studied were quenched to obtain 100 per cent. martensite. The paper includes numerous photomicrographs illustrating the structural features obtained by the etching procedures used.

From the results of the study, the authors conclude that ferrite-grain-growth occurred in the 3140 steel at tempering temperatures immediately below the lower critical temperature, and that this evidence indicates that upper-nose embrittlement should be regarded as the change in impact properties which takes place concomitant with microstructural changes during the fourth stage of tempering. It was found that the visible-light microscope can be employed, at maximum resolution, to detect microstructural features which are normally considered to be beyond the range of the instrument. Investigation of etching practices employed for study of temper brittleness showed that a light polishing after etching destroyed significant structural details, and that, for a given steel, using etchants of picric-acid base, the same degree of etching attack can be induced in un-embrittled specimens as is exhibited by embrittled specimens. Ferrite grain boundaries, as well as prior austenite boundaries, of both embrittled and un-embrittled specimens are heavily delineated.

Influence of Niobium on Temper Brittleness of Low-Alloy Chromium-Nickel Steel

M. P. BRAUN, B. B. VINOKUR and A. I. KONDRASHEV: 'Influence of Niobium on Temper Brittleness of Chromium-Nickel Steel.'

Izvest. Vysshikh Ucheb. Zavedenii, Chernaya Met., 1958, No. 8, pp. 113–26.

The tendency to temper brittleness of a nickel-chromium steel (containing carbon 0·3, nickel 1·5, chromium 1·25, per cent.) was considerably reduced, and impact-resistance increased, by niobium additions in the range 0·3–0·4 per cent. Additions higher than 0·4 per cent. were less beneficial, while lower additions were in certain cases found to be without effect. Particulars of recommended heat-treatments are given in *Chemical Abstracts*, 1959, vol. 53, May 25, p. 8998.

Influence of Temper-Embrittlement on the Fatigue Properties of Nickel-Chromium Steels

E. B. MIKUS and C. A. SIEBERT: 'The Effect of Temper-Embrittlement on the Fatigue Properties and Damage due to Fatigue Overstressing of a 3140 Steel.'

Amer. Soc. Testing Materials, 1959, *Preprint* 67; 10 pp.

The conclusions drawn by the relatively few investigators who have studied the fatigue characteristics of temper-embrittled steel are often in conflict. The investigation now described was carried out in an attempt to clarify the effects of temper-embrittlement on the fatigue-resistance of a low-alloy steel of the following composition: carbon 0·39, silicon 0·28, manganese 0·78, phosphorus 0·01, sulphur 0·019, nickel 1·26, chromium 0·61, molybdenum 0·04, per cent. Two sets of specimens were prepared for testing: specimens of one set were in the toughened condition (tempered for 1 hour at 1250°F. (675°C.)); those of the other set had been severely embrittled by an additional tempering treatment of 500 hours at 850°F. (455°C.), followed by a water quench.

The specimens were subjected to two series of rotating-beam fatigue tests. In the first the S–N curves were established in a conventional manner. The second series was designed to determine the influence, on the run-out life of the specimens, of pre-stressing at a high stress: the specimen was loaded to the required pre-stress for a pre-determined number of cycles, and then, without interruption to the test, was subjected to the lower run-out stress of 75,000 p.s.i. (33·5 t.s.i.; 52·7 kg./mm.^{2}). Fatigue data for tough and temper-embrittled specimens were compared, using statistical methods.

The results of this correlation lead the authors to the conclusion that the mean fatigue strength of the steel in the finite-life region of the S–N curve is not affected by temper-embrittlement. Temper-embrittled structures were found to be more susceptible than tough structures to fatigue damage by periods of over-stress high above the run-out stress, but both tough and temper-embrittled structures tended to be strengthened by periods of over-stress slightly above the run-out stress. The scatter for fatigue life, at a given stress level, was greater for tough than for temper-embrittled specimens. The initiation of damage by pre-stressing above the run-out stress was a function both of the number of cycles at the pre-stress and of the pre-stress level.

Applications of Nickel-containing Materials in the Vehicle Industry

A. W. SHEARER: 'Automotive Applications of Nickel and its Alloys.'

Automotive Industries, 1959, vol. 120, Feb. 15, pp. 54–60, 93–94.

In the years in which the demand for nickel far exceeded supply industry was, wherever at all feasible, forced to use low-nickel or nickel-free steels and alloys in many applications for which materials of

higher nickel content are more suitable. Some of these substitutes have proved satisfactory, but now that supplies of nickel are ample to meet all needs, the advantages offered by nickel and nickel-containing alloys and steels will, it is expected, ensure that the materials will not only consolidate their former uses, but also find a wide range of new applications. In the automobile industry, for example, carbon steels have in some cases replaced low-alloy constructional steels for the rear axles of passenger cars, but in trucks, buses, tractors, farm machinery and construction equipment nickel-bearing steels are extensively used for such applications. The improved availability of nickel has prompted car manufacturers to meet more adequate specifications with regard to the thickness of the nickel coating on plated parts, and it is anticipated that in 1959 the amount of nickel used (for all purposes) per car will increase from an average of 5 lb. (2·2 kg.) to one of 6 lb. (2·7 kg.). This article is concerned with present and potential applications.

After classifying the various types of nickel and nickel-containing alloys and steels, correlating them with their principal applications, and tabulating the forms in which the high-nickel alloys are commercially available, the author discusses typical applications in passenger cars and farm equipment (wheel-type and crawler tractors) and construction equipment (off-highway and crane-mounting trucks, and two-wheel tractors). The text is supplemented by cut-away and other diagrams illustrating the components in, for example, a truck-axle assembly for which nickel-containing materials are used.

Resistance to Embrittlement of Cadmium-Plated Nickel-Chromium-Molybdenum High-Strength Steel

P. N. VLANNES, S. W. STRAUSS and B. F. BROWN: 'Progress in the Development of a Non-Embrittling Cadmium Electroplating Process.'

Plating, 1959, vol. 46, May, pp. 467–8.

The paper gives details of the exploratory phase of an investigation designed to develop a cadmium-plating process which would not induce the susceptibility to embrittlement exhibited by ultra-high-strength steels cadmium-plated from conventional cyanide solutions.

Fatigue specimens of A.I.S.I. 4340 nickel-chromium-molybdenum steel, heat-treated to strengths in the range 285,000–300,000 p.s.i. (127–134 t.s.i.; 200–211 kg./mm.^{2}) were cadmium-plated to a thickness of about 0·0007 in. (0·0175 mm.), using the following types of electrolyte:

(*a*) an ammoniacal cadmium-sulphate solution containing the ammonia salt of glycine;

(*b*) a methanol solution of cadmium acetate;

(*c*) an aqueous tri-ethanolamine cadmium-sulphate solution; and

(*d*) the standard cyanide bath.

Some of the specimens plated from the methanol and tri-ethanolamine solutions were over-plated with cadmium from the cyanide bath, and some of those from the cyanide bath were coated with two deposits of cadmium, with interpolation of a baking treatment between the two. The plated specimens were tested to fracture in a tensile machine, and susceptibility to embrittlement was assessed on the basis of reduction-in-area. The results presented indicate that specimens plated from the glycinate, methanol and tri-ethanolamine solutions are embrittled to a far lesser degree than those from the cyanide electrolyte.

Vacuum Deposition of Cadmium Deposits

D. J. FISHLOCK: 'Vacuum-Evaporated Cadmium Deposits.'

Electroplating and Metal Finishing, 1959, vol. 12, June, pp. 221–2, 224.

The article gives details of a vacuum-deposition technique (the 'Vac-Ca..' process) developed by an American company, Anadite Inc., as a means of cadmium plating ultra-high-strength steels without the risk of hydrogen embrittlement associated with conventional cadmium-plating techniques.

The 'Vac-Cad' process resembles that used principally for vacuum deposition of aluminium. Depending on the plating conditions, the complete processing cycle, including pumping down and actual evaporation, requires only 15–30 minutes for deposition of a 0·5-mil coating of cadmium. The only heat source required is that for evaporation, and at no time does the temperature of the components exceed 80°C. The steel is prepared for plating by sand blasting, preceded, when necessary, by degreasing. Adhesion and corrosion-resistance of evaporated cadmium deposits are stated to be equal to those of electroplated coatings, though their density is slightly less.

The article includes data derived from tensile tests on specimens of a low-alloy nickel-chromium steel heat-treated to a strength of 260,000 p.s.i. (115 t.s.i.; 182 kg./mm.^{2}) and cadmium-plated either electrolytically or by the 'Vac-Cad' process. The specimens were coated with 0·3–0·5 mil of cadmium, and tested within four hours of plating. Using reduction-in-area as a criterion of embrittlement, those specimens which had been vacuum-plated exhibited no loss in ductility, while those electroplated were embrittled to various degrees.

Charpy Impact Testing: The Low-Blow Transition Temperature

G. M. ORNER and C. E. HARTBOWER: 'The Low-Blow Transition Temperature.'

Proc. Amer. Soc. Testing Materials, 1958, vol. 58, pp. 623–34; disc. pp. 634–9.

Complementary to a long-term experimental programme initiated to evaluate and improve the Charpy impact test, a procedure (the 'low-blow technique') has been developed which permits determination of

the maximum temperature at which a crack can become self-propagating. The account of the technique contained in the present paper is based on the detailed information available in individual reports to which reference is made (see, for example, abstract of a paper by ORNER in *Nickel Bulletin*, 1958, vol. 31, No. 8, p. 226).

The technique, which requires initiation of a crack by means of a low-energy blow and propagation of the crack by a full-capacity blow of the impact-machine pendulum, is described in terms of data obtained from tests on 3 per cent. and 9 per cent. nickel steels. Advantages are stated to be:

(1) Crack-initiation and crack-propagation stages of fracture may be separated.

(2) Using a fundamental definition of transition temperature, the technique permits determination of a crack-propagation transition temperature which is essentially independent of notch and specimen geometry. Thus, by means of the low-blow technique, standard V-notch and keyhole Charpy specimens indicate the same transition temperature.

(3) By re-cooling the specimen before striking the crack-propagating blow, adiabatic temperature-rise effects associated with the crack-initiation stage of fracture are essentially eliminated in so far as they affect brittle-crack propagation.

HEAT- AND CORROSION-RESISTING MATERIALS

Precipitation in 'Nimonic 90' at Temperatures above the Ageing Temperature

T. GEIGER and R. KOLLRACK: 'Electron-Microscopical Investigations on the Heat-Resisting Alloy 'Nimonic 90'.'

Schweizer Archiv, 1959, vol. 25, Apr., pp. 111–16.

X-ray-diffraction studies of age-hardening in nickel-chromium-base alloys similar to those of the 'Nimonic' series have indicated that hardening is not due to the stable $Ni_3(Al,Ti)$ phase (i.e., the γ' phase), but is rather the result of the metastable intermediate phases which occur in the supersaturated solid solution. MANENC (*Revue de Métallurgie*, 1957, vol. 54, pp. 161–8) found that the stable γ' phase occurred only after prolonged exposure to the ageing temperature, in a condition which was partly over-aged. The present investigation was intended to supplement the previous X-ray investigations by an electron-microscopical study of the sub-microscopical structural changes which occur in this type of alloy during relatively short-time annealing at temperatures above the optimum age-hardening temperature (700°C.).

Specimens of 'Nimonic 90' taken from fully-aged gas-turbine blades were soaked at 800°, 900° and 1000°C. for periods of 5 minutes, 15 minutes, 30 minutes, 1 hour or 25 hours, and then water-quenched. Hardness measurements were made, and the structure of each specimen was subjected to electron-microscopical examination.

In its initial condition the structure of the alloy was characterized by the presence of γ' precipitates in a matrix which contained some of the age-hardening elements (Al and Ti). These precipitates in the form of unstable intermediate phases, could not be conclusively identified by electron microscopy but appeared to act as the actual bearers of the age-hardening effect. When material in this condition was exposed to temperatures above 700°C., the unstable intermediate phases incorporated coherently in the lattice were replaced by heterogeneous precipitated particles. With rise in temperature the rate of precipitation and the number of particles produced increased, and when the duration of treatment was prolonged the precipitation process gave way, as the temperature range approached the region of the solidus of the γ' phase, to a process of coalescence and dissolution.

The decrease in hardness resulting from the precipitation and distribution processes occurring above 700°C. was independent of the number and size of the precipitates present. The precipitation of γ' particles indicated an over-ageing effect, and the steady loss of hardness was apparently due to the transformation, into more stable but less effective precipitates, of the slip-inhibited foreign atoms incorporated in the lattice. The temperature-dependence of this process was of more significance for the fall in hardness than the number, size and distribution of the precipitates formed. Since even electron-microscopical study permitted only indicative identification (in the form of etch pits) of the actual carriers of the age-hardening effect, the authors advise that literature data relating to slip-inhibiting effects of microscopically or electron-microscopically visible precipitates should be approached with caution.

Precipitation from Solid Solution: Educational Lectures

See abstract on p. 245.

Influence of Retained Austenite on Precipitation Reactions in Age-Hardenable Steels

G. KRAUSS and B. L. AVERBACH: 'Retained Austenite in Precipitation-Hardening Stainless Steels.'

Trans. Amer. Soc. Metals, 1959, vol. 52, *Preprint* 134; 12 pp.+ figures and tables.

The principal mechanism involved in the hardening of precipitation-hardenable stainless steels is that of transformation of austenite to martensite, but further substantial increases in hardness are induced by subsequent ageing of the martensite. The investigation described was carried out to clarify the rôle played by retained austenite in the hardening and precipitation reactions of two chromium-nickel steels: one of 17-7 type containing 1 per cent. of aluminium, the other of 17-4 type containing 3 per cent. of molybdenum. In some precipitation-hardening steels there appears to be no change in

the retained austenite during ageing, whereas in others contraction observed after ageing is attributed to a slight reversion of the martensite to austenite. Reversion of the martensite to austenite in the aluminium-containing steel is reported to begin at ageing temperatures above 1076°F. (580°C.), while it has been suggested that the retained austenite in the molybdenum-bearing steel decomposes on cooling from the tempering temperature, to give increased hardness.

In the present investigation the aluminium-containing steel was solution-treated at 1750°F. (955°C.) and the molybdenum-bearing steel at 1850°F. (1010°C.). They were then hardened by the two procedures in general use: (1) heating, in the case of the former steel, at 1425°F. (775°C.) and, in the case of the latter, at 1350°F. (735°C.), to achieve an austenite→martensite transformation on cooling to room temperature, or (2) refrigeration at −100°F. (−73°C.) to convert the martensite to austenite. Both treatments were followed by an ageing treatment in the range 700°-1100°F. (370°-595°C.). The amount of austenite retained in the steels after the various heat-treatments was determined by X-ray-diffraction techniques.

The austenite contents of the steels in the solution-treated condition were relatively high (in the region of 60-80 per cent.). Subsequent heat-treatments, however, reduced the amount of retained austenite to 7-10 per cent. Ageing increased the austenite present in the aluminium-containing steel, and it appeared that the increase in hardness associated with the ageing treatments was caused by a precipitation reaction in the martensite. The formation of martensite on cooling from an intermediate temperature, or on refrigeration treatment, appears to be the primary hardening mechanism in the 17-4-Mo steel, and the small changes in hardness observed on ageing are probably due to formation of additional martensite.

Chi Phase in the Iron-Chromium-Nickel-Titanium System

H. HUGHES and D. T. LLEWELYN: 'χ Phase in the Fe-Cr-Ni-Ti System.'

Jnl. Iron and Steel Inst., 1959, vol. 192, June, p. 170.

Since the observation of a phase designated χ was first reported by ANDREWS (*Nature*, 1949, vol. 164, p. 1015), the literature has included references to its occurrence in Fe-Cr-Mo and Fe-Cr-Mo-Ti alloys. Kasper concluded that the phase was of an ordered α-Mn type. With one exception (in the Fe-Cr-W ternary system), molybdenum appears to have been present in the iron alloys in which the χ phase was identified, and titanium appears to promote the formation of the phase.

The authors' short communication relates to the discovery, in an Fe-Cr-Ni-Ti steel (carbon 0·026, silicon 0·42, manganese 0·54, chromium 24·9, nickel 4·1, titanium 3·48, aluminium 0·037, per cent.), of a phase with the same X-ray pattern as χ phase and α-Mn. Chemical analysis of a residue obtained from a specimen heat-treated for 120 hours at 850°C. indicated that the χ phase might be allocated a formula $Fe_{35}Cr_{13}Ni_3Ti_7$, compared with $Fe_{32}Cr_{16}Mo_{10}$ according to Andrews, and $Fe_{36}Cr_{12}Mo_{10}$ used by Kasper. A residue extracted from a steel prepared to the suggested composition, and subjected to the same heat-treatment, proved to consist predominantly of χ phase, with a small amount of hexagonal Laves phase based on Fe_2Ti. The results establish that χ phase can occur in titanium-containing alloy steels free from molybdenum.

Diffusion of Iron in Nickel-base Alloys

See abstract on p. 253.

Correlation of the Stress-Rupture Properties of the 'Nimonic' Alloys

H. CONRAD: 'The Correlation of the Stress-Rupture Properties of the 'Nimonic' Alloys'.

Jnl. Inst. Metals, 1959, vol. 87, June, pp. 347-9.

In the light of experimental and theoretical support for the idea that high-temperature deformation is diffusion-controlled, the author has proposed a rupture equation of the following form:

$$t = C \exp\left(\frac{\Delta H}{R\,T}\right) f(\sigma,\ T)$$

where t is the time to rupture, C is a constant, ΔH is an activation energy associated with the diffusion of the base metal or one or more of the alloying elements, R is the gas constant, T is the temperature, and $f(\sigma, T)$ represents the stress function.

BETTERIDGE, in an evaluation of several common time-temperature parameters, as applied to extrapolation of data on 'Nimonic 80A' and 'Nimonic 90' for $t < 3{,}000$ hours, found that the smallest average deviation from the observed stresses for rupture times greater than 3,000 hours was given by the Manson/Haferd parameter (*ibid.*, 1957-58, vol. 86, Jan., pp. 232-7; *Nickel Bulletin*, 1958, vol. 31, No. 4, p. 109). In the present paper the author (using the data given by Betteridge) compares predictions based on his proposed equation with those previously obtained with the Manson/Haferd parameter.

It is concluded that the ability of the equation to predict stresses for rupture times of up to 34,000 hours from test data of less than 3,000 hours' duration is good; deviation from the experimental data is comparable to that of the Manson/Haferd parameter and less than that of other parameters in common use. It is shown that the Manson/Haferd parameter represents a special form of the proposed equation, which would account for the agreement between the two.

Boron-containing 'S-816' Cast Turbine-Blading Alloys

W. J. WATERS, R. A. SIGNORELLI and J. R. JOHNSTON: 'Performance of Two Boron-Modified 'S-816' Alloys in a Turbojet Engine Operated at 1650°F.'

U.S. Nat. Aeronautics and Space Administration, Memorandum 3-3-59*E*, Mar. 1959; 30 pp.

Previous investigations had shown that a 1 per cent. addition of boron, though deleteriously affecting ductility, increased the stress-rupture life of the cobalt-base turbine-blading alloy 'S-816', to an extent which indicated that the modified form of the alloy would exhibit satisfactory strength at operating temperatures in the region of 1650°F. (900°C.): see reference to report by BLATZ *et al.* in *Nickel Bulletin*, 1956, vol. 28, No. 9, p. 151. Subsequently, by increasing the chromium and cobalt contents and decreasing the nickel content of the so-called 'S-816'+B alloy, further improvements in stress-rupture strength were achieved. The present report is concerned with evaluation of the suitability of these two alloys (the compositions of which are shown below) for use as turbine blades at an operational temperature of 1650°F. In view of the low ductility of the materials, particular attention was paid to impact-resistance during operation.

Twenty-six blades were cast from each alloy and installed in a turbo-jet engine which was operated at repeated cycles of 15 minutes at rated speed (11,539 rev./min.) and 5 minutes at idle speed (4,000 rev./min.). At rated speed the mid-span portion of the blade, where stress-rupture failure is most likely, was subjected to a temperature of 1650°F. (900°C.) and a nominal centrifugal stress of 18,900 p.s.i. (8·5 t.s.i.; 13·3 kg./mm.^{2}). In all cases, however, fracture occurred near the tip of the airfoil, and failure in the mid-span portion during operation had to be artificially induced by sawing partially through the blade. Supplementary to the engine tests, tensile and impact tests were carried out at room temperature and 1650°F., and stress-to-rupture tests were run at the latter temperature under stresses in the range 18,000–40,000 p.s.i. (8–17·8 t.s.i.; 12·5–28 kg./mm.^{2}).

Although in room-temperature impact tests both alloys exhibited only limited ductility, impact-resistance was considerably higher at 1650°F. Blade failures began after 10 hours of engine testing, and thereafter occurred at various intervals during the 107½-hour test: the lives of the blades were short relative to those predicted on the basis of stress-rupture considerations (280 hours for 'S-816'+B and 1750 hours for the modified 'S-816'+B). No significant difference was observed in the performance of the two series of alloys.

Mechanical fatigue was found to be the primary cause of failure in both alloys: impact damage occurring as a direct result of fatigue failures in the blade tip was a secondary cause. Small pieces from the fractured tips caused a relatively large amount of damage in the surrounding blades of both alloys. The amount of impact damage due to fractures induced at the mid-span region of the blade was no greater than that which occurred as a result of tip failures.

See also

Thermal-Fatigue Cracking of 'S-816' and 'M-252' Gas-Turbine Blading

J. R. JOHNSTON, J. W. WEETON and R. A. SIGNORELLI: 'Engine Operating Conditions that Cause Thermal-Fatigue Cracks in Turbojet-Engine Buckets.'
U.S. Nat. Aeronautics and Space Administration, Memorandum 4-7-59*E*, Apr. 1959; 24 pp.

To establish the failure mechanism involved in leading-edge cracking of gas-turbine blades during service, and to determine the operational conditions which contribute to such failure, a series of engine tests was run, using blades fabricated either from the cobalt-nickel-chromium alloy 'S-816' or the nickel-chromium-cobalt-molybdenum alloy 'M-252'.

The tests were conducted under the following conditions: (1) a steady-state run under full-power conditions; (2) rapid cycling between idle and rated speed; (3) start/stop cycling with five minutes at idle speed before each stop; (4) start/stop cycling with 15 minutes at rated speed before each stop; (5) start/stop cycling involving gradual starts and normal stops with 5 minutes at idle speed before each stop.

The primary cause of leading-edge cracking was found to be thermal fatigue produced by repeated starting of the engine. The leading edge of the bucket experiences plastic flow in compression during starts, and is consequently subjected to a tensile stress when the remainder of the bucket becomes heated and expands. Crack initiation was accelerated when rated-speed operation was added to each normal start/stop cycle, an effect which is attributed to localized creep damage; embrittlement resulting from over-ageing might also have been a contributory factor in this respect. It was demonstrated that leading-edge cracking can be prevented simply by ensuring that the engine is started gradually.

Alloy	Co %	Ni %	Cr %	W %	Mo %	Nb/Ta %	C %	B %	Si %	Mn %	Fe %
'S-816'	44	20	20	4	4	4	0·4	—	0·6	1·20	5 max.
'S-816'+B ..	bal. (43)	20	20	4	4	4	0·4	1	0·4	1·0	3 max.
Modified 'S-816'+B ..	bal. (53)	5	25	4	4	4	0·4	1	0·4	1·0	2 max.

Development of Improved Nickel-base High-Temperature Alloys

J. C. FRECHE and W. J. WATERS: 'Exploratory Investigation of Advanced-Temperature Nickel-base Alloys.' *U.S. Nat. Aeronautics and Space Administration, Memorandum* 4-13-59*E*, May 1959; 39 pp.

Improvements in the efficiency of gas-turbine engines are to a great extent contingent on the use of higher operating temperatures, the achievement of which is, in turn, rendered feasible only by the development of materials of construction with the properties necessary for satisfactory service under the more severe conditions. Load-carrying capacity, oxidation-resistance, impact-resistance, and a high strength/weight ratio are, in particular, pre-requisite for turbine-blading alloys. A survey of the literature confirmed the extensive research which has been undertaken by various investigators, in an attempt to develop nickel-base alloys which would satisfy these requirements. Reference is made in the report to, *inter alia*, work by GUY (*Trans. Amer. Soc. Materials*, vol. 41, 1949, pp. 125-36; see abstract in *Nickel Bulletin*, 1948, vol. 21, No. 11, p. 168), and by KINSEY and STEWART (abstract in *Nickel Bulletin*, 1950, vol. 23, No. 11, p. 214). The aim of the investigation now reported was the development of nickel-base blading alloys suitable for use at operating temperatures in the region of 1800°F. (980°C.), an aim which preliminary studies suggested might best be achieved by exploration of the composition regions defined by Guy and by Kinsey and Stewart.

Kinsey and Stewart achieved strength and adequate oxidation-resistance without the use of chromium, by employing a large amount of molybdenum (21-22 per cent.) and a large amount of aluminium (7·76-8·36 per cent.) as the major alloying elements. Guy, on the other hand, introduced a considerable amount of chromium (12-15 per cent.), together with a much smaller quantity of molybdenum (5-6 per cent.) and a slightly smaller amount of aluminium (5·5-7 per cent.). Minor additions of niobium, iron, manganese, silicon and boron are also present in 'Guy alloy', and minor additions of carbon, iron and silicon are included in the alloy developed by Kinsey and Stewart.

Trial melts of likely compositions modified from these two base types were evaluated by stress-rupture tests, and this work culminated in the production of an alloy exhibiting fair stress-rupture properties, good oxidation-resistance and, a factor of prime importance, offering promise of further development. Its nominal composition is given as molybdenum 8, chromium 6, aluminium 6, zirconium 1, wt. per cent., balance nickel. This alloy then formed the basis for subsequent determination of the effects of the additions shown in the table, which were designed to establish the efficacy of such strengthening mechanisms as complex - carbide hardening, dispersion hardening, and solution hardening.

Addition	%
Boron	0·2, 0·4, 0·6
Carbon	0·125, 0·25
Titanium	1, 2
Titanium + carbon	1·5 + 0·125
	2·0 + 0·125
	2·0 + 0·25
	2·5 + 0·25

The basic nickel content of the alloy was decreased by a percentage equal to that of the particular addition.

The properties of the alloys, which were produced by induction-melting and investment-casting techniques, were determined by: stress-rupture tests, mainly at 1800°F. (980°C.) and 15,000 p.s.i. (6·5 t.s.i.; 10·5 kg./mm.²); tensile tests (on the basis alloy and its 1·5 Ti/0·125 C modification) at room temperature; swaging tests; metallographic examination; hardness measurements. All the alloys, except that containing 0·4 per cent. boron, were subjected to stress-rupture and impact testing, in both the as-cast and homogenized conditions. In most cases, the alloys were homogenized at the maximum temperature which did not cause melting at the grain boundaries.

Full particulars are given of the test conditions and procedures used. The data obtained are presented in detail.

Most of the alloys studied displayed rupture lives of 100 hours or more. The strongest alloy in this connexion proved to be that containing 1·5 per cent. titanium and 0·125 per cent. carbon, the rupture lives of which, in the as-cast and the homogenized conditions, were, respectively, 384 and 574 hours. A slightly lower life was attained with as-cast specimens of alloys containing 2 or 2·5 per cent. titanium + 0·25 per cent. carbon.

Almost all the alloys tested exhibited good impact-resistance: the maximum impact-resistance recorded for the as-cast condition was more than 62·5 in.-lb. This value was obtained with several of the compositions studied, and the impact-resistance of others was only slightly less. Homogenization treatments were not invariably beneficial. The minimum impact-resistance of virtually every alloy in the series is considered to be more than adequate for turbine-blading requirements: alloys exhibiting room-temperature impact-resistance only one-fifth to one-tenth of that of the highest values obtained in the present investigation are currently in service as blading material.

All the alloys studied cracked during swaging, but the presence of only minor cracks in some containing titanium or carbon additions, and the fact that fair results were obtained with the basis alloy, suggest that several of the compositions might, with further modification, become satisfactorily workable.

Although no specific tests were run to determine oxidation-resistance, it was apparent that no undue

oxidation occurred during any of the stress-rupture tests.

It is concluded that, of the modifications studied, the 1·5 per cent. titanium/0·125 per cent. carbon alloy offers most promise for further development.

Influence of Hot Working on Creep Properties of Nickel and 'A-286'

A. P. COLDREN and J. W. FREEMAN: 'An Investigation of the Relationship between Microstructure and Creep-Rupture Properties of Heat-Resistant Alloys.' *Wright Air Development Center, Tech. Report* 58-204, July 1958; 63 pp.

Previous investigations by EWING and FREEMAN had demonstrated that the creep and rupture strengths of a heat-resisting alloy could be appreciably improved by controlled amounts of hot working (see abstract in *Nickel Bulletin*, 1957, vol. 30, No. 9, p. 170). The results of other, similar, research on a wide range of materials had led to the general conclusion that working could, depending on the conditions used, have either a strengthening or weakening effect: the data available were, however, insufficient to provide a basis for correlation of high-temperature properties with hot-working conditions.

The investigation now recorded forms the first phase of an experimental programme initiated with the aim of obtaining the basic knowledge necessary to ensure a reproducible improvement in the high-temperature properties of heat-resisting alloys by suitable control of the hot-working conditions. The report is concerned mainly with creep and rupture data determined as a function of hot-working conditions. Preliminary microstructural studies are described, but correlation of structure with properties will form the subject of a subsequent report.

Two materials were selected for study. One, 'A' nickel, was chosen as representative of a material of simple microstructure, in which extraneous reactions, such as precipitation, are reduced to a minimum. The other, the complex nickel-chromium austenitic steel 'A-286' (carbon 0·06, silicon 0·47, manganese 1·35, nickel 25·3, chromium 14·58, molybdenum 1·38, vanadium 0·21, titanium 2·0, aluminium 0·17, boron 0·004, per cent.) typified an age-hardenable material, in which the effects of hot working would persist after subsequent heat-treatment.

Two types of rolling schedule were used for each material, approximating, respectively, to isothermal working conditions (involving two rapid passes) and to commercial practice (three to six passes without re-heating) in which the last stage of hot-working is usually carried out over a range of falling temperatures. The 'A' nickel was tested in the as-rolled condition: the 'A-286' steel was solution-treated and aged after rolling. Rolling temperatures, reductions-in-area, and test conditions are summarized in the table below.

The data obtained are presented *in extenso*. The authors' summary of their conclusions is quoted below.

''A' Nickel

The results obtained for 'A' nickel indicate that unidentified factors over and above strain-hardening govern properties at 1100°F. (595°C.) and that at 800°F. (425°C.) these factors are about as influential as strain-hardening.

In general, the properties at 1100°F. appeared to be mainly a function of degree of reduction, independent of the initial or final temperatures of working. Recrystallization during rolling or during testing were the two limitations on this generality. At 800°F., the degree of reduction was still an important factor, although the increased influence of strain-hardening made properties more dependent on the temperature of working.

For a given as-worked hardness, the properties at both temperatures increased markedly with temperature of working up to 1600°F. (870°C.). There appeared to be little difference in properties for working at 1600° or 1800°F. (980°C.) on the basis of hardness. Higher strengths at higher hardness levels

Hot-Rolling and Test Conditions for 'A' Nickel and 'A-286'

Material	Initial Rolling Temperature	Reduction in Area %	
		Isothermal	Falling Temperature
'A' Nickel ..	80°, 1400°, 1600°, 1800°F. 27°, 760°, 870°, 980°C.	0. 5, 10, 15, 27, 37	20, 34, 59
'A-286'	80°, 1700°, 1950°, 2200°F. 27°, 925°, 1065°, 1205°C	0, 5, 10, 20, 26, 34	12, 19, 25, 39

	Test Temperature		Applied Stress			Data used in Evaluation
	°F.	°C.	p.s.i.	t.s.i.	kg./mm.²	
'A' Nickel ..	1100	595	20,000	8·9	14	Rupture life; ductility
	1100	595	11,000	4·9	7·7	Minimum creep rate
	800	425	Variable			Stress to produce minimum creep rate of 0·0001% per hour
'A-286'	1350	735	40,000	17·8	28·1	Rupture life; ductility
	1200	650	65,000	29	45·5	Rupture life; ductility
	1200	650	35,000	15·5	24·5	Creep strain *vs.* time curve

for larger reductions were developed by rolling on a falling temperature from 1800° or 1600°F. than could be obtained by nearly isothermal reductions. No direct relationship to grain-size has been observed. The investigation is being continued to determine if the major unidentified factor governing properties is the influence of working conditions on substructures.'

''*A*-286' *Alloy*

'The results for the 'A-286' alloy indicated that the major factor was the temperature of heating for working, and not the degree of reduction or the finishing temperature. The generality of this conclusion is open to doubt, because it may have been due mainly to the prior history of the stock, resulting in initially low strength and very fine grain-size when heat-treated at 1950°F. (1065°C.). In the experiments, working at 1950°F. (1065°C.) gave maximum or near-maximum strengths. Working at 80° or 1700°F. (27° or 925°C.) did not raise strengths much above the low strength of the original stock. Compared to strengths obtained on working at 1950°F. (1065°C.), working at 2200°F. (1205°C.) resulted in slightly lower strength at 1200°F. (650°C.) and slightly higher strength at 1350°F. (735°C.).

'Research carried out under another Air Force contract, on the same 'A-286' stock, indicated that the maximum strength was associated with heating to about 2100°F. (1150°C.). Therefore, the results for working at 1950°F. (1065°C.) probably do not give true maximum strengths.'

Influence of Environment on Creep Characteristics of Austenitic Steels

F. GAROFALO: 'Effect of Environment on Creep and Creep-Rupture Behaviour of Several Steels at Temperatures of 1000°-1200°F.'

Amer. Soc. Testing Materials, 1959, *Preprint* 78; 10 pp.

The influence of environment on creep and creep-rupture strength has been studied by various investigators. SHAHINIAN, for example, found that, for some alloys, environment affects minimum creep rate and notch-rupture as well as creep-rupture behaviour (see abstracts in the 1957 and 1958 volumes of *The Nickel Bulletin*). In the investigation described by the author the creep and creep-rupture properties of a straight-carbon, a chromium-molybdenum and two 18-8-type austenitic steels were determined, *in vacuo* and in a purified mixture of helium + 2 per cent. hydrogen, at temperatures in the range 1000°-1200°F. (538°-650°C.).

The results obtained demonstrated that, within the limits of the test programme, environment has no effect on minimum creep rate or rupture life. At low stress levels a linear relationship was found between log. stress and log. minimum creep rate, a finding which is in agreement with the dislocation-climb theory. A second linear segment was observed at higher stresses. Assuming that the creep rate during secondary creep at low stresses is controlled by dislocation climb and propagation, it would follow that environment would exert little influence on a polycrystalline material, unless there were diffusion of the surrounding medium into the material, to affect these two factors. No such effect was indicated by the results of the study.

Two linear segments were found in log. stress/log. rupture-time plots. The change from the first to the second linear segment coincides with a similar change in the log. stress/log. minimum-creep-rate plots. It is therefore concluded that environment did not affect the interrelation between minimum creep rate and rupture life. At high stress levels, where rupture may be predominantly transgranular, no effect of environment would be expected unless the surrounding medium diffused readily into the material to influence creep behaviour, and hence rupture behaviour. At low stress levels, where rupture is primarily intergranular, excessive oxidation could conceivably decrease rupture life, but, in the present study, oxidation during testing in air apparently did not exert such an effect to any significant degree.

Creep-Rupture of Notched and Un-Notched Specimens of Austenitic Stainless Steel

F. GAROFALO: 'Creep-Rupture Behaviour of Notched and Un-Notched Specimens of Types 304, 316 and 321 Austenitic Stainless Steels.'

Amer. Soc. Testing Materials, 1959, *Preprint* 77; 16 pp.

The paper gives details of experiments designed to determine the effect of notches on the creep-rupture strength of chromium-nickel austenitic steels of 18-8, 18-8-Mo or 18-8-Ti grade (i.e., A.I.S.I. Types 304, 316 or 321). Creep-rupture tests were carried out under various constant initial loads, on notched and un-notched specimens, at 1100° and 1500°F. (595° and 815°C.). In the 18-8-Ti specimens the notch geometry was such as to involve a higher stress concentration factor than in the other two steels. Tests (at 1100°F.: 595°C.) on some of the notched specimens of the same steel were discontinued before rupture occurred, and the specimens were then subjected to metallographic examination, to study the initiation and propagation of rupture.

Using as criterion the ratio of the creep-rupture strength of notched specimens to that exhibited, for equivalent rupture times, by un-notched specimens, it was found that Types 304 and 321 steels are notched - strengthened for short rupture times at 1100°F. (595°C.). For intermediate rupture times a slight notch-weakening effect was evident, but for times greater than 1000 hours both steels exhibited a tendency towards notch-strengthening. At 1100°F. the Type 316 steel was mildly notch-strengthened for all the periods studied. At 1500°F. (815°C.) all three steels were found to be notch-strengthened, Type 321 to the greatest degree, and Type 304 to the least.

Examination of notched specimens of the titanium-stabilized steel, after they had been tested under

load for various times at 1100°F., showed that rupture initiated just below the notch surface, and then propagated both to the notch surface and inward towards the centre of the specimen. After propagating outward to the root of the notch, separation of the newly formed surfaces increases the effective radius at the notch root, whereas propagation of the crack into the interior reduces the effective specimen diameter. The stress-concentration factor is therefore appreciably decreased after initiation and propagation of the initial crack, and it appears that, as a result, the crack travelling inwards is arrested, and an appreciable amount of plastic deformation follows. Such a high degree of localized plastic deformation leads to triaxial tensile stresses at the centre of the specimen, where rupture again initiates. Growth of the internal crack outward completes the rupture process. For the materials tested, rupture was found to be invariably of intercrystalline type.

In un-notched specimens rupture at high stresses appeared to begin predominantly in the centre of the bar, and propagation occurred towards the surface. At low stresses intergranular cracks formed throughout the strained volume, and total separation occurred by propagation and joining of numerous microscopic cracks.

High-Temperature Characteristics of Nickel-containing Intermetallic Materials

R. D. GRINTHAL: 'New High-Temperature Intermetallic Materials. Part VI.'

Wright Air Development Center, Tech. Report 53-190, May 1958; 80 pp.

The report covers the sixth phase (extending from Mar. 1957 to Feb. 1958) of a comprehensive experimental programme planned to evaluate various intermetallic systems in connexion with the search for new high-temperature materials.

The greater part of the work now described relates to the following five systems: Cr-Mo-Ti, Ni-Al-Cr, Ni-Al-Ti, Ni-Al-Zr and Ni-Al-Nb. Test specimens were produced by powder-metallurgical techniques. The report lists the intended and actual compositions of the materials studied and tabulates the results of X-ray analyses, including the phases present, and, wherever possible, lattice constants and X-ray densities. In general, the density, electrical resistivity, modulus of transverse rupture, impact strength, and hardness of the specimens were determined at room temperature. High-temperature properties were determined at 1000°C., and the programme involved measurement of modulus of transverse rupture, 200-hour oxidation tests in air, and (in the case of the first two systems) bend and stress-rupture tests.

The last section of the report is concerned with investigation of a large number of binary rare-earth compounds. In general, only data on X-ray identification are presented, but, whenever it was possible to produce sound samples, information on physical and mechanical properties is also given.

The *Cr-Mo-Ti system* was investigated between the intermetallic compound Cr_2Ti and the molybdenum corner of the equilibrium diagram. From the results obtained, this sector of the system is not considered worthy of further study.

The *Ni-Al-Cr system* was examined only in relation to compositions consisting of NiAl+Cr, and in the nickel-rich portion, and no account was taken of the effect of fabrication variables. Although no fully satisfactory materials were developed (creep- and impact-resistance were inadequate), further study of the system is recommended.

Since the addition of a second phase in equilibrium with NiAl resulted in no significant improvement in properties, an effort was made to increase impact and creep-resistance by addition of titanium, which, it was hoped, would be taken into solution in the NiAl lattice structure. The *Ni-Al-Ti system* was, however, found to contain a large number of binary, and probably some ternary, compounds, none of which was expected to improve impact-resistance.

A brief investigation of the *Ni-Al-Zr system* was conducted to establish whether zirconium would remain in solid solution with NiAl or exist as a binder. X-ray-diffraction analysis showed that up to at least 10 weight per cent. of zirconium (the maximum addition studied in the investigation) is soluble in NiAl. Impact-resistance and strength were improved by the presence of zirconium.

In an attempt to throw light on the hypothesis attributing the improvements in the Ni-Al-Zr materials to lattice distortion resulting from introduction of the large zirconium atom, the *Ni-Al-Nb system* was investigated. The niobium atom (which is smaller than the titanium or zirconium) was taken into solution by the NiAl lattice, but appeared to have no beneficial effect.

From the results of the experiments with nickel aluminide it is concluded that solid-solution strengthening offers a promising avenue of approach. Atoms larger than those of zirconium (for example, magnesium or thorium) may prove beneficial if taken into solution by the nickel aluminide. The effects of such additions on other properties, such as oxidation-resistance, would, however, also have to be taken into account.

Gas-Lubrication of Nickel-containing Materials at High Temperature

D. H. BUCKLEY and R. L. JOHNSON: 'Halogen-containing Gases as Boundary Lubricants for Corrosion-Resistant Alloys at 1200°F.'

U.S. Nat. Aeronautics and Space Administration, Memorandum 2-25-59*E*, Mar. 1959; 27 pp.

Adequate lubrication of components of aircraft and missile power plant becomes increasingly difficult with rise in operating temperatures to the range 500°-1000°F. (260°-540°C.): the effectiveness of organic liquid and grease lubricants is limited to temperatures below 1000°F. Work has therefore been in progress to investigate the feasibility of using thermally stable gases as lubricants, particularly

halogenated gases, such as CF_2Cl_2, CF_2Br_2 and CF_2Br, which are stable in contact with metal surfaces at 1000°F. Where metals are in sliding contact, the flash temperatures generated at contacting asperities can be as much as 600C.° higher than the ambient temperature. Such temperatures are sufficient to rupture the chemical bonds of gases adsorbed on the surface, and the metallic halides formed by reaction with the surface material then function as solid lubricants and are continuously re-formed when needed. The object of the research reported by the authors was two-fold: (1) to determine the resistance of various high-temperature materials to corrosion by such gases, and (2) to study the lubrication of suitably corrosion-resistant materials in the presence of one or more of the following gases: CF_2Cl_2, CF_3Br_2, CF_3Br, CF_3I, I_2 and SF_6.

Corrosion tests in the most corrosive of the atmospheres used (a mixture of CF_2Cl_2 + 1% SF_6) were carried out at 75°, 600° and 1200°F. (25°, 315° and 650°C.) on the following materials: 'M-1' tool steel, straight-chromium stainless steel; 'L' nickel, cast 'Inconel', 'Inconel S', 'Inconel X' nickel-silicon alloy (Si 7½ per cent.), 'G' nickel, 'Hastelloy C', 'Hastelloy R-235'; 'Multimet', 'Stellite 21', 'Stellite 98M2', 'Stellite Star J'; molybdenum; titanium; and the nickel-containing cermet 'K-162B Kentanium'. Of the materials tested, the nickel-base alloys (particularly the nickel-silicon alloy, 'Inconel X' and 'Hastelloy C') showed little or no corrosion.

Lubrication tests were conducted, at temperatures ranging from 75° to 1200°F. (25°-650°C.), using apparatus consisting essentially of a flat-surfaced rotating-disc specimen sliding, at a velocity of 120 ft./min. (36 m./min.), against a hemispherically tipped rider specimen under a load of 1200 gm. 'M-1' tool steel, 'Stellite 98M2' and 'Hastelloy C' were used for the discs; the rider specimens were fabricated from 'M-1' tool steel, 'K162B Kentanium', 'Stellite 21', 'Stellite 98M2' 'Inconel X' and the nickel-silicon alloy.

The authors' summary of the results obtained is quoted below:

'(1) Corrosion-resistant alloys were lubricated effectively by reactive gases at temperatures from 75° to 1200°F. (25°-650°C.). The best material/gas combinations with regard to friction, wear, and corrosion-resistance varied with the temperature level. Thus, the optimum conditions for gas lubrication are highly selective.

'(2) Bromine-substituted gases were effective lubricants for nickel-base alloys (e.g., 'Hastelloy C'). A good lubricant for 'Stellite 98M2' riders and 'Hastelloy C' discs, over the entire temperature range, was CF_2Br_2. Especially effective from a wear standpoint, at temperatures below 600°F. (315°C.), was CF_2Br_2. Monobromotrifluoromethane + SF_6 gave very low wear from 800° to 1200°F. (425° to 650°C.). Mixtures of the gases may have merit.

'(3) Chlorine-substituted gases were especially effective lubricants for cobalt-base alloys (e.g., 'Rexalloy 33').

'(4) The addition of SF_6 as a minor (1 per cent. by volume) constituent in gaseous mixtures with chlorine or bromine-substituted methane derivatives was generally beneficial. The additive improved the surface-film-formation properties of the other gases so that run-in at low-temperature operation was less critical.

'(5) Iodine and an iodine-substituted gas were found to afford surface protection up to 1000°F. (540°C.), for a nickel alloy sliding on a cobalt alloy. No advantage was gained, however, with the iodine-containing gas that cannot be obtained with a bromine- or chlorine-substituted gas.'

Thermoelectric Stability of Nickel and Nickel-Alloy Thermocouple Materials at Elevated Temperatures

J. M. BERRY and D. L. MARTIN: 'Thermoelectric Stability of Thermocouple Materials at Elevated Temperatures.'
General Electric Research Laboratory, Report No. 55-RL-1234, Mar. 1955; 28 pp.

The findings of previous work by the authors had indicated that during the life of a thermocouple a series of inhomogeneities occur which are associated with the temperature and time of exposure. The pattern of inhomogeneity along the thermocouple is determined by the temperature distribution which obtains in the relevant region of the furnace, and consequently any change either in the position of the thermocouple or in the temperature gradient will be reflected in changes in the thermal e.m.f. In the present report the authors first describe a technique developed for study of the thermoelectric stability of thermocouple materials at elevated temperatures, and then present the results of such tests on two grades (one bright, one oxidized) of, respectively, the nickel-aluminium alloy 'Alumel' and the nickel-chromium alloy 'Chromel'; on the nickel-copper alloy 'Copnic; on commercial and high-purity grades of nickel; on fine and high-purity silver; and on palladium.

Wire specimens of these materials were isothermally aged at 780°C. for various times, some *in vacuo*, to permit account to be taken of the oxidation effects resulting from ageing in air. After ageing, each specimen was evaluated as one leg of a platinum/specimen thermocouple, in tests in which the thermal e.m.f. was measured, using the temperature of melting zinc or of water/steam equilibrium as reference points.

The results obtained by means of this technique are considered by the authors to offer a more suitable criterion for evaluation of thermoelectric stability than criteria obtained by testing the materials under gradient conditions. The isothermal data can, moreover, be used to estimate errors in temperature measurement which might arise from use of combinations of the tested materials in thermocouples.

Some of the materials exhibited relatively large changes in thermoelectric properties as a result of exposure at elevated temperatures in air. On the other hand, the high-purity grades of nickel and silver were found to be quite stable in air at 780°C., and a

thermocouple made from a combination of the two metals proved relatively insensitive to changes in temperature distribution, even after long periods of use.

The data indicated that a stabilizing treatment at the service temperature, prior to use, would considerably improve the stability of most of the materials, and other results suggest that such an improvement could be rapidly attained by stabilizing treatments at temperatures somewhat higher than those to which the thermocouple would be exposed. No definite conclusions were reached with respect to the influence of high-temperature oxidation (as opposed to thermally induced metallurgical effects) on thermoelectric properties, but the amount of 'scatter' exhibited by the data obtained from the vacuum-aged specimens suggests that the maintenance of a bright appearance offers no assurance that a so-called 'protective' atmosphere is effective in preventing changes in thermoelectric properties.

Influence of Boron on the Properties of Cast Austenitic Steels

R. W. KRAFT and R. A. FLINN: 'The Rôle of Boron in Cast Austenitic Alloys.'

Trans. Amer. Soc. Metals, 1959, vol. 52, *Preprint* 133; 17 pp. + figures and tables.

A review of the literature showed that the data available, while confirming the beneficial effects of boron on austenitic steels, gave little information on the structural changes underlying these effects. Experiments on cast austenitic steels had indicated that their elevated-temperature properties improved continuously with increase in boron content, and, in view of the fact that the influence of boron can be determined over a much wider range of contents in cast steels than is possible in wrought grades (due to the forging difficulties associated with boride formation), the investigation described in the present paper was limited to a study of cast specimens of relatively simple 18-8 type chromium-nickel steels.

Test bars were produced by vacuum-melting and -casting techniques, and the boron additions ranged from 0·1 to 5 per cent. The mechanical properties of the steels in the as-cast condition were determined at room temperature, and stress-rupture and creep tests were carried out at 1500°F. (815°C.) on as-cast specimens and on specimens which had been heat-treated at 2150°F. and 2200°F. (1175°C. and 1205°C.). The effects of pre-stressing at room temperature before creep testing were also taken into account. The results of metallographic studies involving use of electron-microscopical and X-ray-diffraction techniques are fully reported.

It was found that boron contents greater than 0·3 per cent. resulted in the formation of significant amounts of complex borides which reduced elongation at room temperature to less than 5 per cent. On the other hand, tensile and stress-rupture properties at 1500°F. (815°C.) improved continuously with increase in boron content, and elongation was little influenced.

Metallographic examination showed that in the as-cast specimens boron was present not only as a gross precipitate, but also in matrix regions, though the data did not indicate whether the boron existed in solid solution, concentrated in vacancies, or as extremely fine borides unresolved by the electron microscope. The boron in the matrix increased as the total boron content was raised, despite the fact that a gross boride precipitate was found to be present at a level as low as 0·1 per cent. boron. This conclusion was substantiated by the finding that increasing amounts of boron precipitated from the matrix as a result of a spheroidizing high-temperature heat-treatment. During creep testing a boride precipitate appeared in the matrix regions of as-cast specimens, and the photomicrographs indicated that this boride reduced matrix microcracking, which is one of the main factors contributing to rupture of these specimens at elevated temperatures.

The 'conditioning' heat-treatment at 2200°F. (1205°C.) resulted in precipitation of the 'matrix' boride at sub-grain boundaries during subsequent stressing at 1500°F. (815°C.). This preferred location of the precipitate was associated with a reduction in microcracking and further improvement in elevated-temperature properties. Pre-stressing at room temperature gave cognate effects.

In addition to throwing light on the influence of boron, the specimens tested provided a means of exploring the interrelation of test temperature, metallographic structure, and mode of fracture. The relative importance of the matrix and of the gross brittle grain-boundary precipitate upon strength and ductility is reversed by temperature. At room temperature failure is the result of cracking due to the presence of brittle grain-boundary precipitates: at elevated temperatures, gross deformation and rupture are largely governed by microcrack propagation through the matrix, the brittle gross precipitate merely realigning itself as the matrix flows.

Spreading of Steels during Rolling

See abstract on p. 256.

Alloying of Stainless Steel with Uranium- or Thorium-base Alloys

R. S. NEYMARK: 'Rate of Alloying of Metal Fuels with Stainless Steel above 1500°F.'

Nuclear Engineering and Science Conference, Cleveland, 1959, *Preprint V*-89; 19 pp.

In the Sodium Reactor Experiment (one of the experimental reactors forming part of the U.S. Atomic Energy Commission programme to develop high-temperature nuclear-power reactors) the fuel elements consist of clusters of seven rods enclosed in a 0·01 in. (0·25 mm.)-thick jacket of 18-8 chromium-nickel stainless steel. To facilitate thermal bonding, the annulus between fuel slug and jacket is filled with NaK. During high-temperature operation, the life

of such fuel elements is governed to a great extent by the ability of the stainless-steel jacket to maintain its integrity: were the jacket to alloy with the metallic fuels its wall thickness, and hence its effective strength, would be reduced. To determine the effects of eutectic formation on the life of S.R.E. fuel elements, a study was made of the rate of alloying of stainless steel and uranium- or thorium-base alloys at temperatures in the range 1600°–2300°F. (870°–1260°C.). Particulars of the procedure used and the results obtained are given in the present paper.

The authors summarize their main conclusions as follows:

'The stainless-steel jacket of an S.R.E. fuel element containing uranium-metal fuels will be penetrated rapidly whenever it exceeds about 2000°F. (1095°C.). Melt-through will occur within a few seconds. At 1800°F. (980°C.) the jacket will maintain its integrity for about a minute, while at 1600°F. (870°C.) a life of over three hours may be expected. At normal operating temperatures of about 1000°F. (540°C.) eutectic formation should be extremely slow, too slow to affect the anticipated life of the element.

'Thorium-fueled elements will not be damaged by eutectic formation as quickly as uranium-fueled elements. The iron-thorium eutectic melts at a higher temperature, and the melting point of the fuel is higher than that of the stainless steel. The anticipated life should be over 10 minutes at 1800°F. (980°C.), decreasing to about one minute at 2300°F. (1260°C.). As with uranium fuels, the life of a thorium-fueled element operating at normal temperatures should not be affected by eutectic formation.'

British Specifications covering Nickel and High-Nickel Alloys

HENRY WIGGIN AND CO., LTD.: 'Some Official Specifications for Wiggin High-Nickel Alloys.'

Publn. 1469, 1959; 87 pp.

The publication summarizes the requirements laid down by the various British Standards and D.T.D. specifications (published, respectively, by the British Standards Institution and the Ministry of Supply) which are relevant to high-nickel alloys, in various forms and conditions, produced by Henry Wiggin and Co. Ltd. The stated aim of the brochure is to indicate to designers that many of the Company's products are covered by official specifications, rather than to reproduce the standards. The data quoted are generally minimum requirements: information on the range of properties offered by each material can be obtained from the Company's other publications. Reference to the official specifications is facilitated by retention of the original numbering in the tables quoted in the brochure.

The following materials fall within the scope of the specifications covered: nickel, low-carbon nickel, 'Ferry', 'Brightray B', 'Brightray C', 'Brightray S', 'Monel', 'H Monel', 'K Monel', 'S Monel', 'Inconel', 'Nimonic 75', 'Nimonic 80', 'Nimonic 80A', 'Nimonic 90'.

Nickel-Chromium-(Iron) Electrical-Resistance Alloys: Specification

AMER. SOC. TESTING MATERIALS: 'Proposed Standard Specifications for Drawn or Rolled Nickel-Chromium and Nickel-Chromium-Iron Alloys for Electrical-Heating Elements.'

Contained in Report of Committee B-4 on Metallic Materials for Electrical Heating, Electrical Resistance and Electrical Contacts.

A.S.T.M. Preprint 10, 1959, pp. 4–7.

The standard relates to annealed, drawn or rolled electrical-resistance alloys conforming to the limits of composition given in the table below.

Requirements are specified in sections covering: composition, physical condition and properties; nominal resistivity and tests for resistivity; nominal electrical resistance, and tolerances on electrical resistance, per unit length; resistance change with temperature; durability; finish, packing and marking.

Austenitic Nickel-Chromium-(Copper) Grey-Iron Castings: Specification

See abstract on p. 255.

Properties of Chromium-Manganese-Nickel-Nitrogen Austenitic Steels

K. HAEFNER, A. F. LAHR, W. L. MEINHART and J. J. KANTER: 'Property Relationships of Some Cast and Forged Chromium-Manganese-Nickel-Nitrogen Steels containing 18 per cent. Chromium.'

Amer. Soc. Testing Materials, 1959, *Preprint* 75; 12 pp.

The work reported was initiated following a survey

A.S.T.M. Specification for Electrical-Resistance Alloys

Alloy	*Ni %	Cr %	Mn %	C %	Si %	S %	Fe %
80 Ni-20 Cr	77-79	19-21	2·5 max.	0·15 max.	0·75-1·5	0·01 max.	1·0 max.
60 Ni-16 Cr	57 min.	14-18	1·0 max.	0·15 max.	0·75-1·5	0·01 max.	remainder
35 Ni-20 Cr	34-37	18-21	1·0 max.	0·15 max.	1·0-3·0	0·01 max.	remainder

* Small quantities of cobalt are to be reported as nickel.

of published data which had indicated the need for investigation of the properties of steels containing carbon 0·08, chromium 18, manganese 0–18, nickel 0–8, nitrogen 0–0·5, per cent. The test programme involved determination of austenite/ferrite relationships, the upper limit of nitrogen solubility, forgeability, castability and corrosion-resistance (assessed on the basis of the nitric-acid and acidified-copper-sulphate tests). Tensile, impact and hardness tests were carried out, at room temperature, on wrought and cast grades of each steel, and a study was made of the embrittling effects resulting from heating for up to 1000 hours, at temperatures in the range 800°–1800°F. (425°–980°C.).

From the data presented the authors draw the following conclusions:

'(1) The elements manganese and nickel increase the nitrogen solid-solubility limit.

'(2) The austenite-forming ability of nitrogen, nickel, and manganese decrease in the order stated.

'(3) Gas-free austenitic compositional ranges are made possible by proper balance of the elements manganese, nickel and nitrogen.

'(4) Forging and solution treatment at 2000°F. (1095°C.) reduce ferrite content.

'(5) Manganese has little effect on the corrosion-resistance. Nickel increases corrosion-resistance and shows a marked influence at 4 per cent. and higher. Nitrogen exhibits a dual behaviour, in that it increases the corrosion-resistance as long as its ability to form austenite can be utilized, and lowers it when alloyed into already austenitic structures.

'(6) Manganese shows little influence on mechanical properties of austenitic/ferritic and austenitic steel compositions. Nitrogen increases strength and lowers ductility. Nickel, when alloyed into nitrogen-free steels, increases ductility and lowers strength, but when nickel is alloyed into nitrogen-containing steels, both strength and ductility are lowered.

'(7) Low-nickel compositions containing more than 5 per cent. ferrite show pronounced embrittlement in the temperature range 1000°–1600°F. (540°–870°C.). This is due to changes occurring within ferrite areas prior to, and as a result of, formation of sigma phase from ferrite. With about 15 per cent. ferrite no embrittlement was detected in 1000 hours at 800°F. (425°C.).

'(8) Highly-austenitic steel compositions with a low nickel content suffer embrittlement in the temperature range 1000°–1600°F. (540°–870°C.), due to grain-boundary and lamellar precipitates (Cr_4C or Cr_2N or both).

'(9) Nitrogen-containing steels show, after long-time annealing at 1800°F. (980°C.), a localized precipitation embrittlement.'

Resistance of Austenitic Steels to Intercrystalline Corrosion: Influence of Long-Time Exposure at High Temperatures

H.-J. WIESTER and G. PIER: 'Study of Intercrystalline Corrosion in Austenitic Chromium-Nickel Steels after Long-Time Exposure to Temperatures in the Range 450°–800°C.'

Archiv f.d. Eisenhüttenwesen, 1959, vol. 30, May, pp. 293–7.

Heat-resisting austenitic steels containing 16 per cent. chromium and 13 or 16 per cent. nickel used for steam-boiler tubing are subjected in service to prolonged exposure at temperatures in the range 500°–650°C., i.e., at temperatures capable of inducing 'sensitization' to intergranular corrosion. Though some doubt exists as to whether, and, if so, the degree to which, pressure-vessel water can cause intergranular attack, the authors considered it advisable to determine whether the results of a corrosion test after the conventional sensitization treatment of ½ hr. at 650°C. are a valid criterion of intergranular-corrosion-resistance after long-time exposure to temperatures in the sensitization range. The present paper gives details of the investigation.

Eleven chromium-nickel steels were selected for investigation: four of 18–9 type, with or without titanium or niobium additions; four of 18–10 type containing 2 per cent. molybdenum (unstabilized or stabilized with titanium or niobium); two of niobium-stabilized 16–13 type, one of which contained molybdenum and vanadium; one niobium-bearing 16–16–Mo grade.

The steels were quenched from various temperatures in the range 950°–1300°C. and then held at temperatures of 450°–800°C. for times up to 10,000 hours. Subsequently susceptibility to intergranular corrosion was assessed by tests in a boiling copper-sulphate/sulphuric-acid solution containing copper filings.

The results are summarized in the form of time/temperature / intergranular - corrosion diagrams, in which curves delimit (as a function of the quenching temperature of the steel and the time and temperature of exposure) the region in which sensitization occurred.

It was found that, for a given temperature, all but one of the steels exhibited a more or less extensive period in which sensitization was possible. The exception was an unstabilized steel of 18–10 type with a very low carbon content (0·006 per cent.), which, irrespective of the quenching temperature used, remained resistant to intergranular corrosion after exposure times of up to 10,000 hours in the temperature range investigated. The curves of the temperature/exposure-time diagrams were characterized by two features: an extension of the sensitization zone with rise in quenching temperature, and the tendency of this zone to occur at shorter exposure times, the higher the temperature of exposure.

See also following abstract.

Resistance of Austenitic Steels to Intercrystalline Corrosion: Influence of Precipitation Reactions

H.-J. WIESTER, H.-J. SCHÜLLER and P. SCHWAAB: 'Precipitation Reactions in Austenitic Chromium-Nickel Steels and their Influence on Susceptibility to Intercrystalline Corrosion.'

Archiv f. d. Eisenhüttenwesen, 1959, vol. 30, May, pp. 299–308; disc. pp. 308–9.

The investigation referred to in the preceding abstract provided the present authors with an opportunity of determining the structural changes which had occurred in the steels studied, and hence of attempting some correlation between the precipitation reactions and susceptibility to intergranular corrosion.

Metallographic studies were carried out, using optical- and electron-microscopical techniques, on two steels. The first, chosen as typifying an unstabilized steel, was of 18–9 type containing 0·06 per cent. carbon; the second, a niobium/tantalum-containing 16–13 grade of similar carbon content, was representative of a fully stabilized steel.

The authors discussion of their findings is supplemented by reference to the many photomicrographs which are included in the paper.

Correlation of the microstructural findings with resistance to intergranular corrosion (as reflected in the time/temperature/intergranular-corrosion diagrams) showed that the transition from immunity to sensitivity was invariably associated with the occurrence of $M_{23}C_6$-type chromium carbides, at the grain boundaries. At higher temperatures and longer exposure times, precipitation occurred also within the grain. In the case of unstabilized materials these precipitates were of $M_{23}C_6$ type, but with the stabilized steels they consisted predominantly of the niobium-tantalum carbide MC. After longer exposure times sigma phase was also formed. With the occurrence of intragranular precipitates susceptibility to intergranular corrosion disappeared.

The course of the boundary line in the time/temperature/intergranular-corrosion diagram is explained in terms of the combined effects of dissolved carbon and chromium and of chromium impoverishment caused by precipitation of chromium carbide, an explanation which is held to be valid also for the stabilized steel. During long-time annealing the participation of the stabilizing element is confined to secondary reactions.

Pitting Corrosion in Austenitic Steels

H. GRÄFEN: 'Pitting Corrosion of Austenitic Chromium-Nickel Steels.'

Metalloberfläche, 1959, vol. 13, June, pp. 161–6.

The author discusses pitting corrosion of 18–8-type chromium-nickel stainless steels in the light of data obtained from experiments involving:

1. Pitting-corrosion tests in $MgCl_2$ and $FeCl_3$ solutions containing various additives.
2. Determination of potential/time and current-density/potential curves for steels exposed to various media, particularly to those of low pH.

Consideration is given to the rôle of halogen ions in the rupture of the passive film, the influence of alloying additions on the resistance of austenitic steels to pitting corrosion, and the relationships between pitting and stress corrosion.

From the data obtained it is concluded that solutions containing both halides (with the exception of fluoride) and redox systems with reducible cations which act also as depolarizers are strongly conducive to pitting corrosion. In acidic solutions in which 18–8-type steels are normally active, pitting corrosion can be induced only by anodic polarization or addition of redox systems. Moreover, sufficient oxygen must be present to maintain the passivity of the cathode. Alkalis have an inhibiting effect. Nitrate additions of sufficiently high concentration prevent pitting corrosion in neutral halogenide solutions, the 18–8 specimens becoming passive. In acidic solutions, on the other hand, such additions give rise to metastable passive equilibrium potentials.

Corrosion of Stainless Steel in Sodium

J. M. MCKEE: 'Sodium Corrosion as a Function of Time.'

Nuclear Engineering and Science Conference, Cleveland, 1959, *Preprint* V–114; 20 pp.

The paper gives details of the apparatus and test procedure used by the authors to determine, as a function of time, variation in the corrosion rate of specimens of 18–8–Mo austenitic steel immersed in flowing sodium.

The stainless-steel tabs were suspended in two identical thermal-convection loops, through which sodium was circulated at a maximum temperature of 1575°F. (855°C.) for 5000 hours. A simple gas lock at the top end of the loop enabled the tab to be removed for weighing, without draining the loop or contaminating the solution. Variations in the corrosion rate were determined by periodic measurements of loss-in-weight.

From the average at 500 hours, the corrosion rate of the stainless steel was found to decay, by a factor of 3, to an apparently constant value of 0·5 mg./cm.²/month at 4000 hours. This decay in the corrosion rate is attributed to changes in the steel rather than in the sodium: a 1·3-mil-thick layer of metal was transformed in 5000 hours from austenite to ferrite, presumably due to composition changes. It is assumed that the ferritic layer is more resistant to corrosion by sodium than the austenitic matrix. The type of decay curve obtained is suggested as a useful means of predicting long-term mass-transfer rates in sodium systems at lower temperatures, for example, to assess suitability in relation to the 20–30 years of service life required for sodium cooling systems in nuclear-power reactors. It was found that with a circuit time of the order of minutes the concentration of container metal dissolved in the sodium was essentially constant at all points in the circuit. In sodium thermal-convection loops, a simple diffusion cold trap would limit the oxygen content to 60 p.p.m.

Corrosion of Alkaline Digesters Clad or Lined with 'Inconel' or Stainless Steel

H. M. CANAVAN: 'Current Status of Alkaline Digester Corrosion as Reported by Regional Digester Group.'
Tappi, 1959, vol. 42, Feb., pp. 129A–132A.

The report summarizes the data obtained, and the conclusions drawn, from the third of the periodic surveys of corrosion in alkaline digesters carried out by the Technical Association of the Pulp and Paper Industry.

The information on which the report is based was received from 26 mills, and relates to experience with 182 carbon-steel digesters, 4 digesters lined or clad with 'Inconel', and 8 lined or clad with molybdenum-containing or niobium-stabilized chromium-nickel stainless steels (A.I.S.I. Types 316 and 347).

The critical corrosion area appears, it is concluded, still to be confined to the middle shell, but the increase in the number of reports designating the lower shell as the critical area is tentatively attributed to stainless-steel overlay welding of the middle and upper shells. Charging of liquor was given as the main cause of corrosion in the critical area.

The average corrosion rate for all the digesters, irrespective of type, was 28·9 mils/year; that for the lined and clad digesters only was 8·8 mils/year. On the same basis of calculation, the average corrosion rate for the critical areas of all the digesters was 58·9 mils/year; that for the lined and clad digesters was 8·3 mils/year. The average corrosion rates for the carbon-steel and the lined and clad digesters were, respectively, 30·4 and 8·8 mils/year.

The report includes a short account of the operation of the 'Vidigage' thickness tester, which is used by many of the mills participating in the survey.

Corrosion of Stainless Steel in a Magnesia-base Sulphite Mill

J. E. FINSEN: 'Controlling Corrosion in a Modern Magnesia-base Sulphite Mill.'
Tappi, 1959, vol. 42, Feb., pp. 104–8.

Operational experience in many sulphite mills, and extensive research on the magnesia-base process, had confirmed the suitability of 18-8-Mo stainless steel (A.I.S.I. Type 316) for service involving contact with liquor and acid. To avoid excessive maintenance due to corrosion, and to ensure that metallic contamination of the high-quality dissolving grades of wood pulp should be kept to a minimum, large amounts of the stainless steel were therefore specified for use in the Ketchikan (Alaska) mill of the Ketchikan Pulp Company. Almost immediately after the mill came into operation in 1954, however, premature corrosion failures occurred in fabricated piping and equipment, due, it was established, to the ineffectiveness of the closed system for recovery of chemicals. Chlorides introduced into the system by chips cut from salt-water-borne logs were not only not being removed, but were being concentrated to levels which resulted in premature corrosion of the steel. No practical method of isolating and removing chlorides from the system has yet been evolved, but this paper outlines the measures taken to minimize the various forms of corrosive attack to which the stainless steel was subjected.

Control measures are described in sections relating to equipment liable to suffer the following types of corrosion: pitting, stress-corrosion cracking, intergranular corrosion, crevice corrosion (concentration-cell corrosion), and general corrosion.

Pitting, which was severe in units of the red-liquor evaporators handling concentrated liquor, was reduced to negligible proportions by specifying a minimum molybdenum content of 2·75 per cent. in the replacement steel, and by ensuring that the stainless-steel sheets were not scratched during handling, by passivating the surface of the steel before service, by cleaning the equipment regularly, and by reducing the ion activity of the concentrated liquor by buffering with magnesia.

Stress corrosion in piping was eliminated, in most cases, by modifications in design aimed at minimizing 'flutter' (caused by hydraulic pulsations) and tensile stress (induced by internal pressure).

Preventive measures against intergranular corrosion of the heat-affected zone of welded stainless-steel components involved solution heat-treatments after welding, or, when heat-treatment was not feasible, use of a rapid welding technique, followed by rapid cooling, to limit to about one minute the period for which the steel was exposed to the sensitization temperature during welding. Where maximum resistance to intergranular corrosion was required the extra-low-carbon grades of stainless steel were employed.

Crevice corrosion was most prevalent in the flanged joints of the fabricated piping systems, and in tongue and groove seals. In seams welded on the outside of fabricated pipe, the weld frequently did not fully penetrate the seam, leaving a groove at the weld root which also created ideal conditions for crevice corrosion. The conventional light-weight lap-joint-type flanges were replaced by special heavy cast flanges which, by preventing distortion, and therefore misfit, of either machined or welded gaskets, eliminated any opportunity for formation of concentration cells. The design of tongue and groove seams was also changed to ensure free circulation on all exposed surfaces.

General corrosion, reported as occurring in welds used to lag carbon-steel surfaces with stainless-steel sheet, was attributed to weld dilution, and was satisfactorily reduced by laying down a minimum of three full passes of weld deposit.

Apparatus for Testing Susceptibility to Intergranular Corrosion

G. F. TISINAI and C. H. SAMANS: 'Additional Studies with an All-Glass Multiple-Test Apparatus for Nitric-Acid Testing of Stainless Steels.'
A.S.T.M. Bulletin, 1959, No. 238, May, p. 64.

In 1956 ALGER *et al.* gave details of an all-glass apparatus designed to determine the resistance of stainless steels to intergranular corrosion, using

boiling 65 per cent. nitric acid as the corrosive medium (see abstract in *Nickel Bulletin*, 1956, vol. 29, No. 8-9, p. 177). In the investigation now recorded this same apparatus was employed to establish whether (*a*) the corrosion rate of steels normally highly resistant to the boiling acid would be influenced if such specimens were tested simultaneously with others exhibiting lower corrosion-resistance, and (*b*) whether the corrosion rate of identical specimens would vary with location in the test chamber.

It was intended that specimens of two grades of 18-8 chromium-nickel stainless steel (A.I.S.I. Types 302 and 304) should be tested in the solution-annealed or the sensitized condition, but the carbon content of the Type 304 grade proved too low to obtain a sensitized structure. Forty specimens of the two steels were subjected either to the annealing or sensitization treatments, and were evaluated simultaneously in the multiple-test apparatus. Comparative tests were run on single specimens, in accordance with the A.S.T.M. procedure laid down for the standard Huey test.

The data presented show that specimens tested in the multiple-test apparatus corroded more slowly than those tested in single flasks. This effect was particularly noticeable in the highly-corroded sensitized samples of Type 302 steel; the average corrosion rate of these specimens was about ten times the highest reported by ALGER *et al.* No correlation could be found between rate of attack and location in the test chamber, and the severe bubbling action at the top of the chamber caused no increase in corrosion rate, relative to values obtained at the bottom of the chamber, where the bubbling action was comparatively mild.

Cadmium Plating of Stainless Steel over a Nickel Undercoating

L. DOMNIKOV: 'A New Economic Method of Treatment of Stainless Steels prior to Cadmium Plating from Conventional Cyanide Solutions.'

Plating, 1959, vol. 46, May, pp. 481-3.

The investigation described was concerned with the development of a treatment which would solve the problem of removing the oxide film from the surface of stainless steel prior to cadmium plating.

The various relevant pickling treatments reported in the literature were used by the author without success. Subsequent investigations were therefore confined to determining the feasibility of pre-plating the steel, in a solution sufficiently acidic to remove the oxide film, with a metal which would serve as a suitable basis for deposition of cadmium. Procedures and solutions for electrodeposition of satisfactory undercoatings of nickel and copper are described. The economic advantages inherent in producing the desired undercoating by an electroless process induced the author to carry out further research with this aim. The process finally evolved is outlined in the next column.

The steel is prepared by the following treatments:

(1) Cleaned in an alkaline cleaner at 190-210°F. (90°-100°C.), at a current density of 50-100 amp./sq. ft. (5·4-10·8 amp./dm.^{2}), for 45 seconds anodically, followed by 30 seconds cathodically, followed by 45 seconds anodically.

(2) Rinsed in cold water.

(3) Dipped in 25 per cent. fluoboric-acid solution for 5 seconds at room temperature.

(4) Rinsed in cold water.

The specimen is then treated in a hot (165°F.: 72°C.) 35 per cent. sulphuric-acid solution for two minutes without the application of current. A black film of finely divided carbon is formed on the object during the sulphuric-acid treatment. (The film can be easily wiped off.)

Following this immersion-activation process, the steel object is given a flash of nickel in an immersion bath of the following composition:

	oz./gal.	*g./L.*
$NiCl_2.6H_2O$	8·0	49·9
Boric acid	5·5	34·3

The immersion time is one minute, the temperature of the bath 160°F. (71°C.), and the pH 4·3-4·7.

Upon removal of the object from the nickel bath, it is given a quick rinse, followed by a cyanide dip in a solution containing 6 oz./gal. of sodium cyanide, and is then cadmium-plated in a cadmium-cyanide solution. The carbon film is not soluble in the cyanide but is included in the cadmium deposit. Following cadmium deposition, the object is given a supplementary chromate treatment.

The method is claimed to be simple and economical, and the results of salt-spray tests on cadmium coatings deposited on straight-chromium stainless steel, after electroless pre-plating with nickel or electrodeposition of a nickel or copper flash, demonstrated the superior corrosion-resistance of the cadmium coatings deposited over an electroless-nickel undercoating. The adhesion of the cadmium deposits was excellent, irrespective of the pre-plating treatment used.

Influence of Carbon Content on the Corrosion-Resistance of Austenitic Steel Welds

M. W. MARSHALL: 'Corrosion Characteristics of Types 304 and 304L Weldments.'

Welding Jnl., 1959, vol. 38, June, pp. 247s-50s.

Many metallurgists with experience of the extra-low-carbon grades of the A.I.S.I. series of 18-8-type stainless steels report that their low carbon content renders them sufficiently insensitive to carbide precipitation to ensure immunity, in the as-welded condition, to intergranular corrosion in the heat-affected zones. On this basis, the extra-low-carbon Type 304L* steel is selected in preference to the Type 304 grade (which differs in composition only in its carbon content of 0·08 max. per cent.) for service

* Carbon 0·03 max., silicon 1·0 max., manganese 2·0 max., sulphur 0·03 max., phosphorus 0·045 max., chromium 18-20, nickel 8-12, per cent.

under conditions conducive to intergranular attack. Other metallurgists are of the opinion that Type 304 stainless steel can be safely used in the as-welded condition for similar applications, provided that the relationship of the carbon content and the thickness of the steel is maintained as follows:

Thickness		*Carbon content*
in.	cm.	%
½ max.	1·25 max.	0·06 max.
¾ „	1·9 „	0·05 „
1 „	2·5 „	0·04 „

The present report, compiled under the aegis of the High Alloys Committee of the Welding Research Council, presents the conclusions formed from a review of recent literature, which was undertaken in an attempt to determine the validity of these two apparently conflicting views.

The information is summarized in sections covering the mechanism of carbide precipitation, methods of preventing sensitization (post-weld solution-annealing treatment, stabilization, and use of steels of low carbon content), influence of the corrosive environment, and corrosion-resistance of the weld metal.

The literature survey produced no evidence in support of the view that Type 304 steel could, provided the carbon-thickness relationship was suitably controlled, be used without risk of attack. On the contrary, it was reported that Type 304 steel with a carbon content higher than 0·035 per cent. exhibited high corrosion rates in boiling 65 per cent. nitric acid after sensitization for a short period. (The literature contained no reference, however, to service failures, by intergranular corrosion, of Type 304 steel with carbon contents in the range 0·04–0·06 per cent.) Abundant evidence was available on the high intergranular-corrosion-resistance of the extra-low-carbon grade.

The majority opinion is that the small amount of carbide precipitation in the heat-affected zones of welded stainless steels of normal carbon content can (even at carbon levels as low as 0·04 per cent., and particularly where the severity of the service conditions is unknown) adversely affect corrosion-resistance. The extra-low-carbon Type 304L is regarded as the logical choice for such applications.

Corrosion of Molybdenum-containing Austenitic-Steel Welds

M. E. CARRUTHERS: 'Weld Corrosion in Type 316 and 316L Stainless Steels and Related Problems.'

Welding Jnl., 1959, vol. 38, June, pp. 259s–67s.

Following the suggestion that the High Alloys Committee of the Welding Research Council should undertake research into the corrosion of ferrite-containing weld metals of A.I.S.I. Types 316* and 316L† stainless steels, a questionnaire requesting details of corrosion experience was sent to 106 correspondents in the chemical, fabricating and metal-producing industries, with a view to making a preliminary assessment of the problem. Forty-three replies were received, and the information contained in them is summarized in the present report in the form of 31 tabulated case histories.

The data received are discussed mainly in relation to the corrosion behaviour of the two grades of weld metal in welded-and-heat-treated and as-welded equipment. The questionnaire, however, also threw some light on measures which have been found successful in eliminating corrosion in as-deposited 18–8–Mo weld metal. Data derived from accelerated corrosion tests are briefly outlined, and reference is made to the results of corrosion tests on experimental weld deposits in various grades of stainless steel.

Consideration of the information supplied leads the Committee to the conclusion that research on Types 316 and 316L ferrite-containing weld metals does not appear to be necessary, since weld-corrosion problems are surmountable by post-weld annealing or by a stabilizing heat-treatment. Reference is made below to the other principal findings of the survey.

The performance of Type 316 and 316L welds which had not been subjected to heat-treatment was found to depend upon the severity of the service conditions. The weld failures were in all cases associated with preferential attack at delta-ferrite boundaries. In several cases failure occurred by intergranular corrosion in the heat-affected zones of Type 316 sheets and plates.

Satisfactory corrosion-resistance was reported to have been obtained by repairing pitted Type 316L weld metal with a Type 310 coated electrode (carbon 0·25 max., silicon 1·5 max., manganese 2·0, sulphur 0·03, phosphorus 0·045, chromium 24–26, nickel 19–22, per cent.).

Type 309–Nb electrodes were used to weld Type 316L plate exposed in service to media highly corrosive to Type 316L weld metal. (The composition of Type 309 steel differs from Type 310 as follows: carbon 0·2 max., silicon 1·0 max., chromium 22–24, nickel 12–15, per cent.)

Molybdenum-containing Type 310 weld metal proved resistant to corrosion in boiling 65 per cent. nitric-acid solution, but was preferentially attacked when used to repair welded Type 316L stainless steel exposed to hot 10 per cent. nitric-acid/3 per cent. hydrofluoric-acid solution.

Brazing of Stainless Steel to Copper

M. LIEBSON: 'Brazing Stainless Steel to Copper.'

Rev. Scientific Instruments, 1959, vol. 30, May, pp. 369–70.

In development work on electron tubes it is often necessary to braze copper to stainless steel, an operation normally carried out by plating the steel with a protective coating of nickel and then brazing in an atmosphere of dry hydrogen. This note gives particulars of a brazing technique which

* Carbon 0·08 max., silicon 1·0 max., manganese 2·0 max., sulphur 0·03 max., phosphorus 0·045 max., chromium 16–18, nickel 10–14, molybdenum 2·0–3·0, per cent.

† Composition identical with that of Type 316, except that carbon is limited to 0·03 per cent. max.

obviates the need for a hydrogen atmosphere, for prior to nickel plating, or for fluxing.

The parts to be joined are first cleaned, using standard degreasing and cleaning procedure, and are then assembled with an appropriate solder or bonding material. The temperature of the assembly is raised, *in vacuo*, to the liquefaction point of the solder, and the work is then allowed to cool, still *in vacuo*. The joint so obtained is stated to be vacuum-tight, free from stain, and clean.

The equipment used is illustrated, and the following points are emphasized:

(1) To avoid oxidation, the initial vacuum should be of the order of 10^{-5} mm. of mercury.

(2) To ensure that the entire assembly is at a uniform temperature during brazing, the assembly should be held for 3–5 minutes at a temperature just below the melting point of the solder.

(3) Where the stainless steel has been passivated, the surface to be joined must be machined before brazing, to remove the passivated layer.

Three types of bonding material were used: a gold and copper solder containing 37·5 per cent. gold (melting point 1025°C.); a gold-copper solder containing 80 per cent. gold (melting point 880°C.); and titanium hydride (observed liquefaction 950°C.). The different melting points of these bonding agents enabled various portions of the assembly to be brazed at different times, with no adverse effect on the joints already made.

Electroless Nickel-Phosphorus Alloy for Brazing Stainless-Steel Fuel Elements

P. P. KING and R. K. McGEARY: 'Braze-Bonding Stainless-Steel Fuel Elements for Nuclear Reactors.' *Welding Jnl.*, 1959, vol. 38, June, pp. 241s–6s.

Among the problems encountered in fabrication of multiple-tube sub-assemblies of fuel elements intended for use in pressurized-water reactors has been that of obtaining, without seriously restricting the flow of the coolant, a rigid bond between the individual 18–8-type chromium-nickel stainless-steel fuel elements comprising the sub-assembly. Of the fabrication techniques considered by the authors, mechanical joining and welding were rejected in favour of brazing, and an extensive test programme was initiated to determine suitable brazing alloys and procedures. The present paper gives details of the investigations.

The brazing alloys selected for screening tests were evaluated on the basis of five criteria: corrosion-resistance in water at 650°F. (345°C.), low neutron-capture cross-section, acceptable irradiation behaviour, ductility and strength at the service temperature, and possession of flow temperatures in the range 1800°–1925°F. (980°–1050°C.). Corrosion-resistance was determined by (1) qualitative screening tests in static neutral water at 650°F. (345°C.); (2) determination of quantitative corrosion rates for stainless-steel sandwich specimens brazed with the most promising alloys, and correlation of the data with those obtained for the 18–8; and (3) subjecting brazed tube-bundle specimens to simulated service tests in a dynamic pressurized-water loop at 600°F. (315°C.).

Of the following six nickel-base alloys investigated, only the nickel-silicon and the nickel-silicon-phosphorus alloys proved unacceptable for high-temperature service:

Ni-12P,	Ni-18Cr-9Si,	Ni-13Cr-10P,
Ni-12Si,	Ni-5Si-6P,	Ni-26Fe-4Mo-12Si-4P.

In the corrosion tests the brazing alloys were applied in paste form, but this method was found to have undesirable features and further research was carried out. The results showed that electroless plating offered an ideal means of applying the brazing alloy, a finding which was confirmed by the satisfactory joints obtained with a nickel - phosphorus alloy (containing 8–10 per cent. of phosphorus) deposited by that technique.

The procedure finally developed for 'braze bonding' by electroless deposition of the brazing alloy is fully described by the authors. The alloy coating is deposited, on one of adjacent stainless-steel tubes, to a thickness of 0·0005–0·001 in. (0·0125–0·025 mm.), and, for satisfactory brazing results, the sub-assembly, with the tubes in intimate contact, is then heated in dry hydrogen for 1 hour at 1850°–1875°F. (1010°–1020°C.). The success of the technique is contingent on the component parts' being in sufficiently intimate contact to permit diffusion of phosphorus into the steel, and so, by phosphorus depletion of the brazing alloy, to achieve a ductile single-phase bond. Erosion of the stainless-steel base metal by the brazing alloy was negligible during brazing cycles of up to 8 hours at 1875°F. (1020°C.).

Prototype fuel-element sub-assemblies were successfully fabricated by the braze-bonding procedure, but correct design of the fixture used to pre-position the component parts prior to brazing was found to play a vital rôle in the production of satisfactory joints. The authors describe the brazing fixture developed in their investigation.

(In connexion with the use of electroless nickel as a brazing medium, attention may be directed to work by PATRIARCA *et al.*; see abstract in *Nickel Bulletin*, 1958, vol. 31, No. 5, p. 131.)

Tungsten-Arc Cutting of Stainless Steel

J. D. WAIT and S. H. RESH: 'Tungsten-Arc Cutting of Stainless-Steel Shapes in Steel-Warehousing Operations.'

Welding Jnl., 1959, vol. 38, June, pp. 576–81.

In the last decade demands on steel warehouses have become increasingly more stringent, and warehouse managers have found that, to satisfy the customer, they must not only stock the usual standard lengths and sizes of a wide range of steels, but must also be in a position to supply steel to the exact size and shape required. Following the successful introduction of a pantograph-type machine, equipped with a photo-electric tracer and oxygen torches which permit mild-steel plate to be cut exactly to the customer's

specification, the Morrison Steel Company (with which the authors are associated) decided to develop a cutting technique suitable for similar use with stainless steels. The procedure and equipment finally selected are described in this paper.

Attempts to apply the available oxygen-cutting facilities to powder cutting of stainless steel were relatively successful, but not ideally so. After further intensive research the decision was taken to adopt the tungsten-arc cutting process which, by modification of the existing equipment, would be adaptable for use in conjunction with the electronic shape-cutting head. For the shielding gas, use was made of a mixture of 65 per cent. argon and 35 per cent. hydrogen.

The tungsten-arc unit in present use is suitable for cutting stainless steel up to 2 in. (5 cm.) thick: operating conditions for various thicknesses are tabulated in the paper. The cutting procedure involves the production of a templet of the required shape. The templet is placed under the electronic tracing head, the arc is then struck, and in operation the movement of the tracing head controls that of the cutting torch. The quality of the cut edges is claimed to be excellent; the kerf wall is smooth, and in most cases requires no further machining or grinding: on plate up to $\frac{3}{4}$ in. (19 mm.) thick a tolerance of at least $\pm 1/16$ in. (1·6 mm.) is possible.

Major difficulties encountered in initial operation of the process were concerned with arc initiation, maintenance of tolerances and square edges, dross removal, and correlation of the position of the workpiece with that of the templet. The author's discussion of the methods by which these problems were solved is followed by an outline of the factors involved in the basic stages of the process. By way of illustrating the scope of tungsten-arc cutting, reference is made in the final section of the paper to some of the many stainless-steel pieces of varied shape and size which have been produced by that means.

Determination of Iron, Chromium and Nickel in Stainless Steels by Fluorescent X-Ray Analysis

W. W. HOUK and L. SILVERMAN: 'Determination of Iron, Chromium and Nickel by Fluorescent X-Ray Analysis.'

Analytical Chemistry, 1959, vol. 31, June, pp. 1069–72.

Methods developed in recent years for the analysis of stainless steels by measurement of fluorescent X-rays entail use of solid-steel specimens of prescribed surface area and finish, and are not suitable for analysis of chips, drillings or powders. In this paper details are given of a modified procedure which offers the following advantages: no specific surface area or finish is required; the weight of the sample (and concentration of the elements) can be reduced several hundred times; the means of addition of internal standards, to eliminate any inter-element effect, or instrumental variations, is simplified; one standard sample is sufficient to obtain a working curve covering many types of material.

The technique involves dissolving 0·5 gm. of stainless steel in 10 ml. of a mixture of nitric and hydrochloric acids, to which several drops of hydrofluoric acid and 8 ml. of perchloric acid are then added. The solution is evaporated to dense fumes of perchloric acid, cooled, and diluted to 100 ml. with water. Approximately 10 ml. of the solution are used to fill the solution cell. The times required to record 25,600 counts or 102,400 counts, for iron, chromium, nickel and the background, are measured, using appropriate counters. The ratios of element to background of the total counts per second for the elements are calculated, and the milligrams of the elements are obtained from the appropriate (milligram per millilitre) working curves previously prepared.

The relative merits of three counting techniques were determined: Geiger, scintillation, and scintillation + pulse-height discrimination. Data derived from determination of iron, chromium and nickel in various types of stainless steel and nickel-chromium alloys are tabulated in the paper. The values obtained using a Geiger counter were within 3 per cent. of those recommended for the National Bureau of Standards samples, and within 1·5 per cent. when a scintillation counter was employed. The addition of the pulse-height-discrimination unit to the scintillation counter reduced the lower limit of detection for iron, chromium and nickel to 5–10 γ per ml. of sample. The standard curves plotted for the stainless steels were found to be equally applicable to chromium-nickel alloys.

ANALYSIS

Titration of Nickel Acetate in Glacial Acetic Acid

See abstract on p. 249.

Photometric Determination of Nickel in Copper-Nickel Alloys

See abstract on p. 250.

Determination of Nickel by Extraction with Coloured Cations

See abstract on p. 250.

Determination of Iron, Chromium and Nickel in Stainless Steel by Fluorescent X-Ray Analysis

See abstract on p. 276.

Corrigendum

NICKEL BULLETIN, 1959, vol. 32, No. 7, p. 210.

Production of Nickel Strip by the Direct-Rolling Process

Line 1, *after* D. K. WORN *add* and R. P. PERKS.

Attention is drawn to the fact that many of the names of materials mentioned in The Nickel Bulletin are *Registered Trade Marks*.

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